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RELIABILITY OF FUSIBLE TIN BOILER PLUGS IN SERVICE

By John R. Freeman, Jr., J. A. Scherrer, and S. J. Rosenberg

ABSTRACT

In cooperation with the Steamboat Inspection Service a study has been made of the reliability of fusible boiler plugs of the type installed in ships boilers under the jurisdiction of the Inspection Service. It has been found that under certain conditions fusible plugs would not operate due to the formation in service of a refractory oxide replacing the tin in the fire end of the plug. Apparatus is described in which plugs may be tested under simulated service conditions. The results of examination and tests of 184 plugs returned from service indicated that 10 per cent of all plugs in service would not operate when and if required. Recommendations regarding specifications and design of plugs to eliminate this dangerous condition are made.

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I. INTRODUCTION

The general rules and regulations provided by the Board of Supervising Inspectors of the Steamboat Inspection Service of the Department of Commerce require that every boiler under their jurisdiction other than boilers of the water-tube type shall be fitted with at least two fusible plugs. These are fitted at various places into the boiler either in the flues, tubes, or combustion chamber, in such a position that they are about 1 inch or more above the dangerous low water level with one end on the fireside and the other end on the waterside.

The fusible plug in its usual form consists of a bronze casing, having an external pipe thread, filled from end to end with a fusible metal or metal composition depending upon the temperature at which it is desired to have it function. As long as the water level in the boiler is maintained above the level of the plugs the temperature of the fusible metal remains below its melting point, but if the water in the boiler falls much below the level of the plug local heating occurs, the fusible filling of the plug melts and is blown out.

Plugs for use in marine boilers are generally of two types, known as an inside or outside type. This distinction is based on the manner in which the fusible plug is placed in the boiler. The inside type of plug is so designed that it is screwed into the boiler shell from the inside of the boiler, whereas the outside type is screwed into the boiler

shell from the outside. Photographs of both types are given in Figures 1 (*a*) and 1 (*b*).

On August 19, 1925, a disastrous boiler explosion occurred on the steamer *Mackinac* near Newport, R. I.

The Bureau of Standards is responsible for the testing of the quality of the tin filling of fusible boiler plugs made to meet the specification requirements of the Steamboat Inspection Service. Accordingly, the latter was requested to submit plugs from the exploded boiler in order to determine their condition and, if possible, whether they had failed to function properly, thereby contributing to the cause of the disaster. Under date of August 31, 1925, two plugs were submitted by the Steamboat Inspection Service which were said to have been taken from the boiler of the *Mackinac*. Examination of these two plugs was made and detailed report submitted to the Steamboat Inspection Service on November 4, 1925.

This examination showed that one of the two plugs was in good condition, that it still met the specification requirements after approximately four months of service, and that it would have functioned had it been heated to the melting point of tin previous to the explosion. The second plug, however, showed evidence of serious deterioration in service.

Special apparatus was devised, described in detail later in this report, in which a plug can be subjected to steam pressures at elevated temperatures simulating service conditions. This plug was tested in this apparatus and although subjected to steam pressure at a temperature of about 340° C. it did not "blow out." It, therefore, probably would not have functioned in service had it been called upon to do so.

A plug in this condition obviously constitutes the very dangerous condition of a false security. In view of this fact, it was believed desirable to investigate in some detail the condition of plugs when removed from service.

In a previous report Burgess and Merica [1] showed the effect of small amounts of impurities, especially zinc, on the reliability of the fusible plugs. It was shown with 0.3 per cent zinc, and probably less, in the tin of the plug that a progressive oxidation occurred from the water end outward eventually forming an interlocking "network" throughout the tin of the filling. This network, due to its high melting point and relative strength, acts to prevent the proper functioning of the plug and so constitutes an actual source of danger rather than safety. As a result of this work the specifications of the Steamboat Inspection Service were changed so as to require that the tin in the filling should contain not more than 0.1 per cent lead and zinc, respectively, and a total impurity content of not more than 0.3 per cent.

In a somewhat later report Gurevitch and Hromatko [2] pointed out some of the precautions necessary in manufacture to prevent contamination of the tin in order to meet the rigid specification requirement that the tin filling shall not contain more than 0.3 per cent total impurity. It was shown that the tin should be poured into the casing at as low a temperature as possible in order to avoid contamination by solution of copper and zinc from the casing if made

[1] Burgess, G. K., and Merica, P. D., An Investigation of Fusible Tin Boiler Plugs, B. S. Tech. Paper No. 53; 1915; Ind. and Eng. Chem, 7, No. 10, p. 824; 1915; Trans. Am. Inst. of Metals; 1915–1921.

[2] Gurevitch, L. J., and Hromatko, J. S., Tin Fusible Boiler Plug Manufacture and Testing, Trans. Am. Inst. Min. and Met. Engrs., 64, p. 227; 1920.

of brass and of copper only if made of bronze. To avoid the danger of contamination with zinc, it was recommended that only bronze, with little or no zinc, should be used for the casing material.

The Steamboat Inspection Service requires that plugs shall be renewed at each annual inspection except in cases where plugs were installed or renewed not more than six months prior to annual inspection, in which case they may be allowed to remain until the next following annual inspection or for a period not to exceed 18 months.

It is often noted when plugs are removed after service that the tin in the fire end has been melted out and rather often the space is found to be partially filled with a hard material resembling oxide. Burgess and Merica noted this in some of the plugs they examined. They suggested that the cause for the tin filling merely melting out at the fire end and leaving no oxide in some cases and being oxidized and remaining in place in other cases was probably due to variations in operating conditions of the boilers, to variations of the kind of coal used, and also possibly in the devices used by engineers in charge to stop up leaky plugs. One instance was cited by them in which plaster of Paris had evidently been used to stop a leaky plug.

The question obviously arises whether the presence of the oxide crust often noted in plugs, sometimes after only a few months' service, would prevent proper functioning. The present investigation was planned to answer this question by actually subjecting plugs in the laboratory to the steam pressures and temperatures at which they are expected to function. The Steamboat Inspection Service was requested to cooperate by sending to the Bureau of Standards plugs removed from service by their inspectors, together with as complete a history as possible of their service records. A total of 184 plugs was examined or tested, the details of which are given in this report.

II. TESTING APPARATUS

Special equipment was designed for the purpose of testing these plugs in the laboratory under simulated service conditions. The apparatus used for the so-called "blow-out" tests is shown in Figure 2 and is illustrated diagrammatically in Figure 3. A pressure of over 200 lbs./in.^{2} and simultaneous temperature of over 300° C. can be obtained. In general, for reasons of safety, the pressure was kept low.

The essential difference between the functioning of a plug in this apparatus and under service conditions is that in service the fire end is undoubtedly at a higher temperature. In the apparatus it is always approximately at the same temperature as the steam or "inside" end. It is believed, however, that this difference would not affect the results, since the functioning of the plug is dependent only upon the melting of the tin, and the manner in which the heat is applied would make little difference.

All plugs were tested in the apparatus with the pressure on the same (large) end as in service.

The pressure gauge was installed only in the later tests. That steam pressure was present throughout any one test was always indicated by slightly opening a safety valve on the top of the boiler. This was always done at the end of any test in which a plug failed to blow.

The temperature of the plug was determined in some cases by inserting a thermocouple in the casing, as indicated in Figure 2. A temperature difference of as much as 80° C. was noted in one instance between the temperature of the steam in the pressure chamber and the temperature of the casing of the plug; the latter was always cooler. In general, however, the temperature difference was much less than this. The difference noted depended largely upon the rate of heating. In case a plug did not blow, the temperature of the pressure chamber was maintained a sufficient length of time to permit a more even distribution of temperature to be established. Also, in all cases where a plug failed to blow, except as noted in Table 1, the tin was found to have been melted during the test which proved

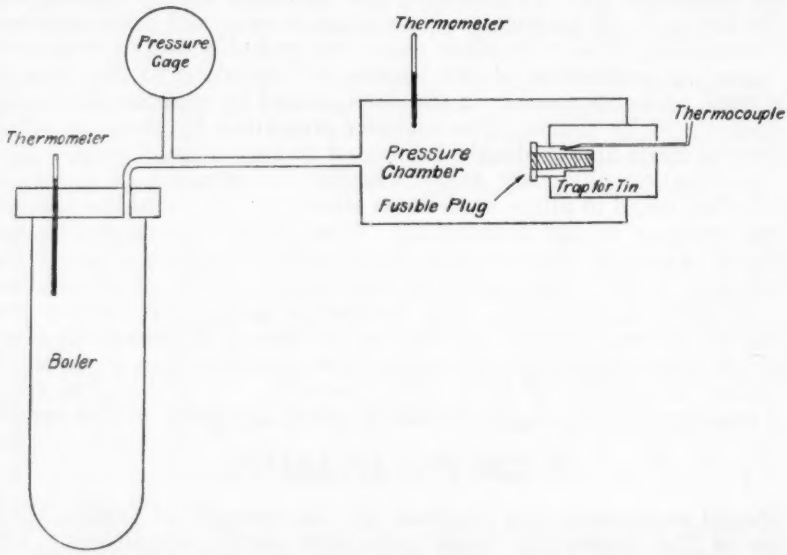

FIGURE 3.—*Schematic representation of testing apparatus shown in Figure 2*

that a temperature greater than the melting point of the filling had been reached.

III. RESULTS OF TESTS

The results of all tests, together with available service data, are given in Table 1. The plug number is that assigned to the plug on receipt from the Steamboat Inspection Service. The heat number is the original number given by the manufacturer. The "condition" is that indicated by inspection on receipt in the bureau laboratory. The data on ships from which plug was removed, type of boiler, boiler pressure and length of service are those given by the inspectors of the Steamboat Inspection Service.

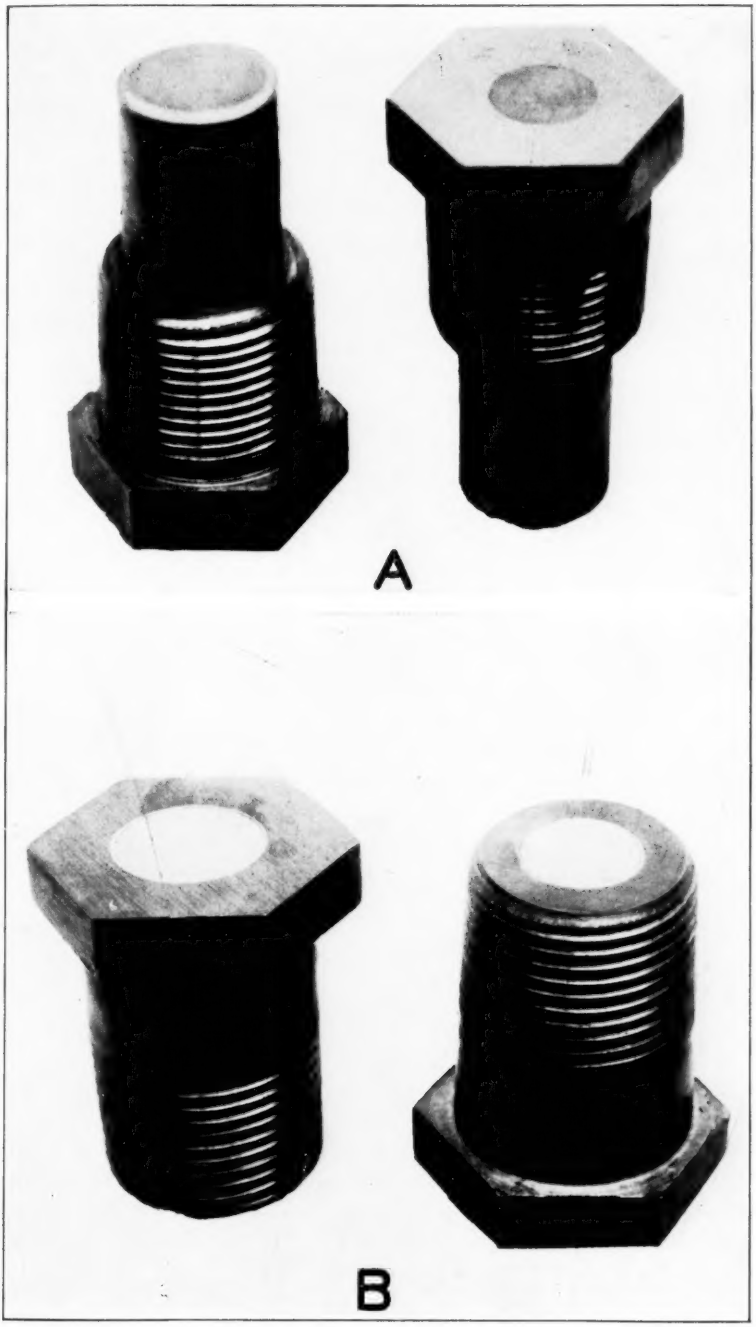

FIGURE 1.—*Fusible tin boiler plugs*

A, Outside type; *B*, inside type.

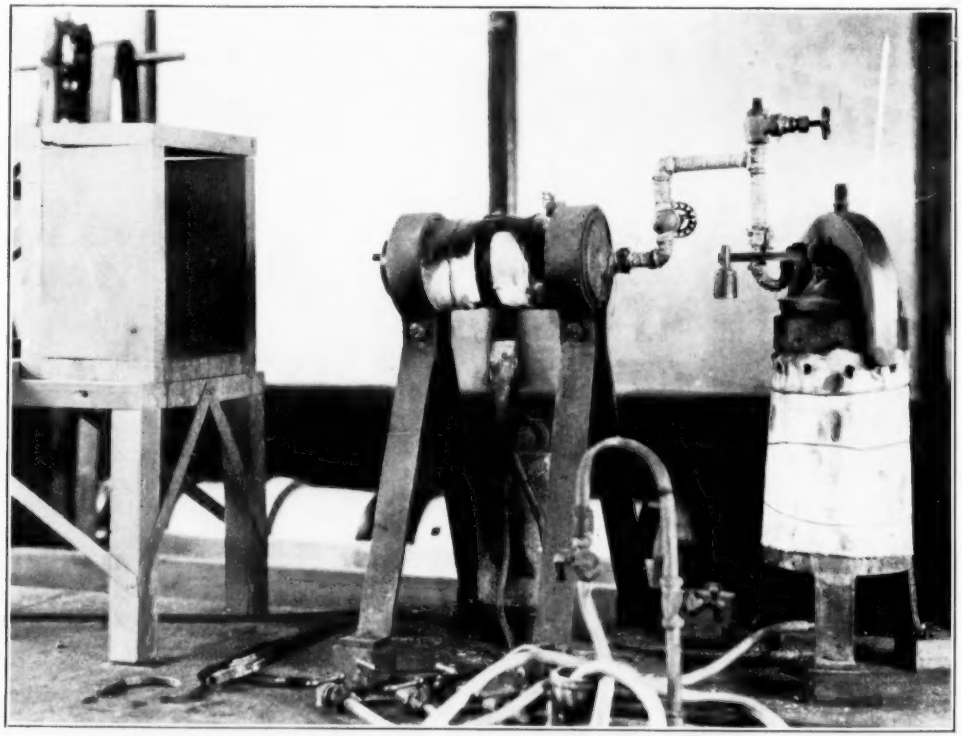

FIGURE 2.—*Apparatus used for testing boiler plugs under simulated service conditions*

TABLE 1.—*Data regarding fusible plugs tested in "blow-out" apparatus*

A. PLUGS THAT FUNCTIONED

Plug No.	Manufacturer	Heat No.	Diameter filling (outside)	Type of plug	Ship	Firing	Time in service	Boiler pressure	Condition of plug	Results	Results of test (temperature of steam at failure) [1]	Pressure of steam at failure
			Inches				*Months*	*Lbs./in.²*			*° C.*	*Lbs./in.²*
1	A	175	½	I					Good	Blew	224	
2	A	170	5/8	O	Albert H. Hill		12	200	About 1 inch melted out of fire end	do	248	
4	A	212	5/16	O	Nora	Oil	12	220	About 3/16 inch melted out of fire end	do	240	
5	A	212	5/16	O	do	do	12	220	About 1¼ inches melted out of fire end	do	244	
6	A	212	5/16	O	do	do	12	220	About 1 inch melted out of fire end	do	239	
7	A	212	5/16	O	do	do	12	220	1⅛ inches melted out of fire end	do	255	
8	A	212	5/16	O	do	do	12	220	Fire end corroded; head almost gone	do	222	
9	A	190	½	I	Walter Franks		12	70	Good	do	242	
10	A	152	½	O	do		12	70	½ inch melted out of fire end	do	217	
11	A	131	½	I	Tug Dixie		12	150	Fire end slightly corroded and burned	do	234	
12	A	131	½	I	do		12	150	do	do	239	
13	A	195	5/8	O	Sun Oil (tanker)		11	190	1 inch melted out of fire end	do	248	
14	A	195	½	O	Tug Shirley Keller		12	125	⅞ inch melted out of fire end	do	245	
15	A	195	½	O	do		12	125	do	do	244	
16	A	194	5/16	O	Federal		12	155	Fire end slightly corroded; water end pushed in about ¼ inch.	do	250	
17	A	208	3/4	O	W. W. Mills		11	210	Fire end slightly corroded	do	262	
18	A	211	5/16	O	Edenton		14	210	1 3/16 inches melted out of fire end	do	241	
19	A	211	5/16	O	do				1½ inches melted out of fire end	do	250	
20	A	209	3/8	O	City of Philadelphia		10	190	5/8 inch melted out of fire end	do	253	
21	A	211	5/16	O	Henry S. Graves		11	220	¼ inch melted out of fire end	do	250	
22	A	211	5/16	O	do		11	220	1 inch melted out of fire end	do	246	
23	A	211	5/16	O	do		11	220	1⅜ inches melted out of fire end	do	243	
24	A	211	5/16	O	do			220	Fire end slightly melted out	do		
26	A	215	5/16	O	Atlantic	Oil	10	210	do	do	249	
27	A	216	5/16	I	Sagadahoe		12	190	Fire end slightly pressed out	do	218	

[1] Figures in parentheses indicate temperature of plug as indicated by thermocouple in the bronze casing.

TABLE 1.—*Data regarding fusible plugs tested in "blow-out" apparatus*—Continued

A. PLUGS THAT FUNCTIONED—Continued

Plug No.	Manufacturer	Heat No.	Diameter filling (outside)	Type of plug	Ship	Firing	Time in service	Boiler pressure	Condition of plug	Results	Results of test (temperature of steam at failure)	Pressure of steam at failure
			Inches				*Months*	*Lbs./in.²*			° *C.*	*Lbs./in.²*
28	A	216	5/16	O	Sabatowan		12	190	Fire end slightly burned	Blew	245	
29	A	216	5/16	O	do		12	190	do	do	248	
30	A	209	5/16	O					Fire end slightly melted out; water end slightly pressed out.	do	217	
32	B	101	15/32	O	L. P. Smith		3	140	1¼ inches melted out of fire end	do	254	
33	B	96	15/32	O	Joseph Medill		8	170	1 9/16 inches melted out of fire end	do	243	
34	B	96	15/32	O	do		8	170	1⅞ inches melted out of fire end	do	251	
35	B	96	15/32	O	do		8	170	1⅛ inches melted out of fire end	do	217	
36	B	106	½	O	Wm. A. Field		4	154	1⅝ inches melted out of fire end	do	215	
37	B	101	½	O	Alex. C. Dinkey		8	170	1¼ inches melted out of fire end head corroded.	do	245	
38	B	106	15/32	O	Harvey		2	150	1⅛ inches melted out of fire end	do	254	
39	B	106	15/32	O	do		2	150	1 inch melted out of fire end	do	250	
40	B	106	½	O	Wm. A. Field		4	154	1½ inches melted out of fire end	do		
41	B	96	15/32	O	Joseph Medill		8	170	1¾ inches melted out of fire end	do	248	
42	B	96	15/32	O	do		8	170	1⅛ inches melted out of fire end	do	246	
43	C	288	3/8	I	Northland	Coal	12	180	Fire end slightly corroded	do	217	
45	C	288	3/8	I	do	do	12	180	Slightly melted out in fire end	do	245	
46	C	288	3/8	I	do	do	12	180	do	do	258	
47	C	189	9/16	O	Federal No. 2		12	155	5/8 inch melted out of fire end	do	240	
48	D	170	½	O	William J. Olcott		8	170	⅞ inch melted out of fire end	do	257	
49	D	173	½	O	Douglas Houghton		8	210	1¾ inches melted out of fire end	do	255	
50	D	161		O	Wm. A. MacGonagle		11	180	⅛ inch melted out of fire end; head almost burned off	do	243	
51	D	173		O	Thomas Lynch		8½	170	2¼ inches melted out of fire end; head badly corroded.	do	245	
53	D	171	½	O	Henry Phipps		9	170	1½ inches melted out of fire end; badly corroded.	do	244	
54	D	171		O	do		11	170	Head burned off; one-half gone from water end.	do		
55	D	161		O	Wm. A. MacGonagle		11	180	Head badly corroded; 1¼ inches only of filling left.	do		

56	E	65	5/16	O	Ocean City Ferry (tug)		12	150	3/4 inch melted out of fire end	do	253
57	E	42		I	Alice		12	110	Excellent	do	213
58	E	97	3/8	I	Curtis Bay		12	150	Good	do	
59	E	97	1/2	I	F. C. Latrobe		3	72	Excellent	do	253
60	E	88	1/2	I	Louie		12	120	Fire end slightly pushed out	do	247
61	E	97	5/16	I	Wilson		12	190	Excellent	do	243
62	E	88	7/16	I	Little Nora		12	240	Fire end slightly pushed out	do	240
63	E	98	1/2	O	F. C. Latrobe		1	72	Excellent	do	260
64	E	90	1/2	O	Annapolis		4	80	do	do	247
65	E	97	5/16	I	Nelson		12	190	Fire end slightly bulged out	do	213
66	E	74	5/16	I	Chickasaw		12	200	Good	do	244
67	E	78	1/2	O	Annapolis		4	80	do	do	203
68	E	97	5/16	I	Nelson		12	190	do	do	
69	E	77	1/2	O	Annapolis		4	80	do	do	
70	F	58	1/2	O	Paulsboro		12	215	1 1/16 inch melted out of fire end	do	231
71	G	57	5/16	I	Middlesex		13	130	Fire end slightly bulged out	do	248
72	G	57	5/16	I	do		13	130	5/8 inch melted out of fire end	do	213
73	G	56	5/16	O	State of Maryland	Coal	2	185	1 inch melted out of fire end	do	253
74	G	56	5/16	O	do	do	2	185	Good	do	258
75	G	56	5/16	O	do	do	2	185	7/8 inch melted out of fire end	do	251
77	G	56	5/16	I	Middlesex			130	Fire end slightly bulged	do	225
78	G	56	5/16	I	do			130	do	do	254
81	H	181	5/16	O	Melville Dollar	Oil	12	210	1 inch melted out of fire end	do	213
83	I	109	1/2	I	Erastus Wells		12	150	Good	do	260
84	I	103	1/2	I	do		12	150	Fire end slightly bulged out	do	240
85	I	106	1/2	I	Bold Eagle		12	198	do	do	256
86	I	106	7/16	I	do		12	198	Fire end slightly melted out	do	259
87	I	106	1/2	I	Gladys	Coal	12	140	Fire end slightly bulged out	do	260
88	I	103	1/2	I	Alabama		12	184	5/32-inch melted out of fire end	do	
89	I	102	1/2	I	Perryville		7	148	Good	do	240
93	E	93	3/16	O	A. Brooke Taylor	Coal	8	150	5/8-inch melted out of fire end	do	
94	E	115	1/2	O	Ridgewood	do	2	125	1 1/4 inches melted out of fire end; removed because leaking.	do	
95	E	115	1/2	O	do				1 1/2 inches melted out of fire end; leaking.	do	
96	A	229	5/16	O	McKeesport		12	210	7/8 inch melted out of fire end	do	
97	A	229	5/16	O	do		12	210	1 3/8 inches melted out of fire end	do	260
98	A	229	5/16	O	do		12	210	1 1/8 inches melted out of fire end	do	
99	A	265	5/16	O	Wytheville		12	210	do	do	
100	A	265	5/16	O	do		12	210	1 9/16 inches melted out of fire end	do	
101	A	265	5/16	O	do		12	210	1 1/4 inches melted out of fire end	do	
105	E	84		O	A. Brooke Taylor	Coal	12	150	Melted out of fire end for considerable distance.	do	240

TABLE 1.—*Data regarding fusible plugs tested in "blow-out" apparatus*—Continued

A. PLUGS THAT FUNCTIONED—Continued

Plug No.	Manufacturer	Heat No.	Diameter filling (outside)	Type of plug	Ship	Firing	Time in service	Boiler pressure	Condition of plug	Results	Results of test (temperature of steam at failure)	Pressure of steam at failure
			Inches				*Months*	*Lbs./in.²*			° *C.*	*Lbs./in.²*
106	E	84		O	A. Brooke Taylor	Coal	12	150	½ inch melted out of fire end	Blew	276 (235)	
107	E	125		O	Ridgewood	do	6	125	do	do	264 (230)	
108	E	115		O	Pioneer	do	12	100	Melted out half length of plug; loose crust in fire end.	do	283 (235)	
110	E	116		O	Ridgewood	do	6	125	Melted out half length of plug; loose crust.	do	310 (230)	
111	D	174		O	Wm. A. MacGonagle	do	8½	180	Heavy crust; water end covered with scale.	do	275 (244)	
115	I	116		I	Gladys	do	12	140	Fire end slightly melted out	do	289 (230)	
116	I	116		I	do	do	12	140	Fire end considerably swelled out	do	300 (245)	
117	A	265		O	Wytheville		8		One-third length of filling melted out	do		144
118	A	265		O	do		8		One-half length of filling melted out	do	269 (233)	105
119	A	265		O	do		8		Crust	do	280 (238)	158
120	A	265		O	do		8		One-fourth length of filling melted out	do	277 (232)	135
121	A	265		O	do		8		One-half length of filling melted out	do	280 (232)	120
122	A	265		O	do		8		do	do	289 (235)	150
123	A	265		O	do		8		Crust fire end	do	285 (231)	70
125	A	265		O	do		8		do	do	286 (230)	100
126	A	265		I	Nelson	Oil	15	190	do	do	282 (233)	125
127	A	220		I	do	do	15	190	do	do	283 (238)	100
129	E	97		I	do	do	15	190	do	do	287 (236)	95
130	E	97		I	do	do	15	190	do	do	288 (236)	98
131	E	97		I	do	do	15	190		do	272 (237)	140
132	G	54		I	do	do	15	190	Crust fire end	do	271 (237)	104
133	G	54		I	do	do	15	190	do	do	281 (235)	100
134	E	63		I	J. H. Riehl	Coal	12	100	do	do	277 (228)	96
135	E	115		O	Howard W. Jackson		12	60	One-fourth length of filling melted out; crust fire end.	do	280 (224)	95
136	E	115		O	do		12	60	do	do	280 (228)	120
137	A	265		O	Micheal Tracy	Coal	4	175	Crust fire end	do	286 (228)	125
138	A	229		O	Cape Cod		12		One-third length of filling melted out; crust in fire end.	do		

139	A	265		O	F. J. Williams	Oil		220	Crust fire end	do	288 (229)	100
140	Unknown			O			8		One-half length of filling melted out of fire end; crust fire end.	do	293 (231)	100
141	do			O	Tug boiler			High pressure	do	do	282 (234)	140
147	do								One-half length of filling melted out; crust in fire end.	do	315 (246)	40
148	D	84							One-half length of filling melted out of fire end; crust fire end.	do	290 (231)	110
149	D	186					2		One-third length of filling melted out of fire end.	do	280 (232)	72
151	D	178		O					Crust fire end	do	290 (224)	62
155	I	116		I	Alabama	Coal	12	184	do	do	260 (232)	40
156	I	116		I	do	do	12	184	do	do	267 (233)	80
159	Unknown			O	Q.-A. Gilmore	do	8	150	One-third filling melted out of fire end	do	298 (244)	86
161	D	178		O	do	do	8	150	do	do	275 (232)	100
165	A	265		O	Nueuo		12		Filling bulged out about 3/16-inch fire end.	do	268 (231)	35
168	Unknown									do	275 (231)	85
170	do			O					One-third filling melted out of fire end	do	282 (232)	24
184	do								One-third filling melted out of fire end; plug removed because of leaking.	do	285 (236)	70

B. PLUGS THAT DID NOT FUNCTION

3	A	212	3/8	O	Nora	Oil	12	220	Corroded slightly at fire end	Did not blow	263	
25	A	215	5/16	O	Atlantic	do	10	210	Tin slightly melted out of fire end; crust in fire end; water end slightly pushed in.	do	268	
31	A	212	5/16	O	Inca	Coal	12	190	3/4-inch melted out of fire end; crust in fire end.	[1]	255	
44	C	288	3/8	I	Northland	do	12	180	Crust in fire end	Did not blow	277	
52	D	173	1/2	O	August Ziesins	do	8	180	1/2-inch melted out of fire end; water end slightly depressed; head corroded and eaten away; crust.	do	(249)	
76	G	56	5/16	O	State of Maryland	do	2	185	Apparently satisfactory, although fire end slightly bulged out; crust became apparent after test.	do	260	
79	H	181	5/16	O	Melville Dollar	Oil	12	210	Apparently satisfactory, but crust became apparent after test.	do	(274)	
80	H	181	5/16	O	do	do	12	210	Same as above, but head slightly corroded.	do	(264)	
82	H	181	5/16	O	do	do	12	210	Fire end slightly corroded and bulged out.	do	(276)	
91	A	244	1/2	O	Mackinac	Coal	4 1/2	142	7/8-inch melted out of fire end; head slightly corroded; crust in fire end.	do	337	

[1] Tin filling probably not heated to melting point of tin during test. "Infusible crust," however, was present, and plug probably would not have functioned had it been heated above melting point of pure tin.

TABLE 1.—*Data regarding fusible plugs tested in "blow-out" apparatus*—Continued

B. PLUGS THAT DID NOT FUNCTION—Continued

Plug No.	Manufacturer	Heat No.	Diameter filling (outside)	Type of plug	Ship	Firing	Time in service	Boiler pressure	Condition of plug	Results	Results of test (temperature of steam at failure)	Pressure of steam at failure
			Inches				*Months*	*Lbs./in.*[2]			° *C.*	*Lbs./in.*[2]
92	E	93	5/16	O	A. Brooke Taylor	Coal	8	150	½-inch melted out of fire end; head slightly corroded.	Did not blow.	261	
102	E	122	½	O	General Mathews	do		158	5/16-inch melted out of fire end; fire end closed up solid with a reddish colored crust.	(1)	262	
103	E	122	5/16	O	Clay Foreman	do	12	150	2 inches melted out of fire end; crust in fire end.	(1)	259	
104	E	122	7/16	O	do	do	12	150	3/16-inch melted out of fire end; reddish crust.	Did not blow.	260	
109	E	115		O	Virginia (ferryboat)	do	12	50	One-half length of filling melted out of fire end.	do	267 (232)	
112	D	174		O	Wm. A. MacGonagle	do	8½	180	Heavy crust; water end covered with scale.	do	304 (275)	158
128	A	220		I	Nelson	Oil	15	190	Crust in fire end	do	305 (276)	68
154	I	116		I	Alabama	Coal	12	184	do	do	271 (240)	114

[1] Tin filling probably not heated to melting point during test. "Infusible crust," however, was present, and plug probably would not have functioned had it been heated above melting point of pure tin.

Almost all of the plugs removed from service showed that the tin in the fire end had been melted out probably back of or close to the plane of the outside surface of the boiler where the cooling effect of the water surrounding the plug prevented melting.

For convenience all plugs that failed to "blow out" under test have been placed in one group (Table 1, B) and those that blew in another (Table 1, A).

It will be noted that the plugs were taken from many different ships. These included tugboats, cargo boats, ferryboats, and ships operating in the Great Lakes. This necessarily included both coal and oil fired vessels and high as well as low pressure boilers. The plugs were made by many different manufacturers and were of different sizes. It is believed, therefore, that the condition of the plugs tested represents a fair cross section of service conditions.

The data show that of the 150 plugs tested in the "blow-out" apparatus 13, or nearly 9 per cent, failed to blow out. Five other plugs (Nos. 3, 25, 31, 102, and 103) also failed to blow, but in these cases the tin was found not to have melted out. Chemical analyses after test showed that they met the specification requirements with the exception of plug 31, this being slightly higher in copper but not sufficient to affect the melting point materially. It is therefore highly improbable that these five plugs were heated to the maximum temperature indicated by the thermometer. A thermocouple had not been installed to measure temperature of casings during test at the time when these plugs were tested. However, as discussed later, a longitudinal section of these plugs showed the presence of an "infusible crust" in the fire end which would probably have prevented them from functioning at the temperature of melting tin. If this is true, the percentage of plugs that failed to function would be increased to 12 per cent. Another point that should be noted, however, is that toward the end of the investigation only plugs showing evidence of the "infusible crust" were tested, as it was believed that those showing no crust would function properly.

A total of 184 plugs were received from the Steamboat Inspection Service and examined. Assuming that the five plugs previously discussed would not have functioned, the data indicate that approximately 10 per cent of the plugs examined would not have functioned in service. The average time in service of all of the plugs examined was 10 months.

The cause of the failure to function was evident in every case. It was always due to the presence of a hard "infusible crust" packed tightly in the fire end of the plug replacing some of the tin filling. In general, this deposit was apparent upon inspection, but in many cases, especially when the tin in the fire end had been melted out for an appreciable distance back into the plug, it was difficult to determine its presence, and in some instances a plug which was apparently in good condition failed to function in test because of it.

The appearance of this so-called infusible crust is shown in Figure 4 (plug No. 91). Figure 4 (*b*) shows the water end of plug No. 91 after test. It is evident that the tin melted during test and the plug would have functioned except for the obstruction which had formed in the fire end during service. This is typical of all plugs that failed to blow out in test.

In plug No. 25 (fig. 5) the tin did not melt out during test, thus indicating, as previously mentioned, that the plug itself was not heated above 232° C., the melting point of pure tin, but the hard deposit in the fire end would very probably have prevented its functioning even had the tin melted out. Similarly in plug No. 3 (fig. 6) the deposit in the fire end probably would have prevented proper functioning.

The cause of the formation of the deposit of "infusible crust" was not at first apparent. Chemical analyses of these deposits are given in Table 2, together with the composition of the tin filling after test in the "blow-out" apparatus.

It will be noted that in most cases the tin after test conforms to the specification requirements for new plugs except for the copper content. The increase in this element is without doubt due to "pick-up" of copper from the casing during test by the tin especially while molten.

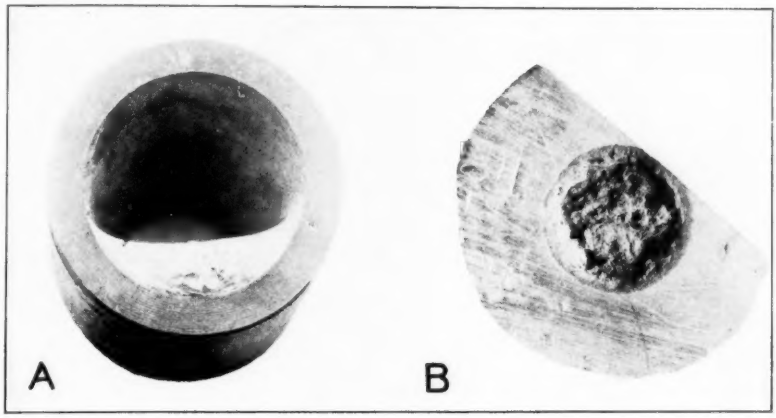

FIGURE 4.—*Plug No. 91 after test*

A, Appearance of water end filling melted during test but "infusible crust" in fire end prevented blowing; *B*, appearance of fire end showing "infusible crust" which had replaced filling during service.

FIGURE 5.—*Section of plug No. 25*

Note crust in the fire end.

FIGURE 6.—*Section of plug No. 3*

Deposit in fire end would probably have prevented functioning.

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TABLE 2.—*Composition of tin filling and "infusible crust" of plugs that did not function in test*

[n. d. = not detected]

Plug No.	Filling (water end)					Infusible crust (fire end)							Remarks
	Cu	Pb	Fe	Zn	Sn (by difference)	SnO_2 (by difference)	Cu [1]	Pb [1]	Fe [1]	Zn [1]	CaO [2]	SO_3	
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cen'*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
8	0.12	0.06	<0.04	n. d.	99.78								
25	.29	.09	< .09	n. d.	99.53	44.0	4.0				22.0	30	Less than 0.1 per cent volatile matter.
31	.48	.10	< .05	n. d.	99.37								
44	.05	.07	< .03	n. d.	99.85								
52	.07	.02	< .04	n. d.	99.87	76.8	2.9	0.2	<0.1	n. d.	8.0	12.0	The $CaSO_4$ may be partially hydrated.
76	.63	.05	< .01	n. d.	99.31	93.85	5.9	.1	< .05	0.1			
79	.22	.27	< .05	n. d.	99.46								
80	.01	.09	< .03	n. d.	99.87	86.71	12.9	.09	< .10	< .20			
82	.15	.12	< .03	n. d.	99.70	80.85	18.4	.50	< .10	< .15			
91	.63	.08	< .01	n. d.	99.28	82.35	5.7	1.3	< .05	.5			SiO_2, 0.20 per cent.
92	.20	.09	< .02	n. d.	99.69	79.6	7.2	1.3	< .20	n. d.	n. d.	11.7	
102	.16	.10	< .02	n. d.	99.72	42.15	44.1	2.5	< .05		4.6	6.6	Crust from fire end of plug.
						86.35	2.8	.3	< .10	< .05	7.3	10.4	Crust from middle of plug.
103	.09	.11	< .02	n. d.	99.78	86.9	10.8	.7	< .2	n. d.	.6	.8	The $CaSO_4$ may be partially hydrated.
104	.18	.02	< .02	n. d.	99.78	94.25	2.2	.25	1.0		1.0	1.3	
109 [3]													
112	.7	.04	.10	n. d.	99.16	79.84	10.0	.04	.10	n. d.	4.0	6.0	Some MgO present probably a sulphate and carbonate.

[1] Present probably as oxides or other compounds, such as $CuSO_4$; not present as metals. [2] Present probably as $CaSO_4$ and $CaCO_3$. [3] Not analyzed.

Chemical analyses were also made of the tin blown out of many of the plugs that functioned properly. The results are given in Table 3. It is evident that, in general, the tin after test conforms to the specification requirements except for the copper content, which undoubtedly increased during test, as discussed later in the report. These data show that the composition of the tin filling does not change in service and that fusible plugs which are free from obstructions, such as the "infusible crust" previously described, may be expected to function when heated to the melting point of tin.

It was thought that the formation of the infusible crust might be associated with certain types of firing or boilers. From Table 1 (B) it is apparent that 12 of the plugs which did not function were used in boilers which were coal-fired and 6 which were oil-fired. Of the plugs that functioned (Table 1 (A), 15 were known to have been in oil-fired and 23 in coal-fired boilers. This indicates that the type of firing has no apparent relation to the formation of the infusible crust.

In Table 4 the plugs have been classified according to the permissible steam pressure of the ship's boilers. The plugs tested were principally from high-pressure boilers. It was, therefore, to be expected that a greater number of the plugs that failed to function would be from high-pressure boilers. The data do not indicate any relation between the crust formation and the pressure of the boilers in which the plugs were used. Data are not available regarding the positions from which the plugs tested were taken.

TABLE 3.—*Composition of tin from filling after test of plugs that functioned*

[n. d.=not detected]

Plug No.	Chemical composition					Plug No.	Chemical composition				
	Cu	Pb	Fe	Zn	Sn (by difference)		Cu	Pb	Fe	Zn	Sn (by difference)
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*		*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
1	0.65	0.02	<0.04	<0.04	99.25	30	0.94	0.06	<0.03	<0.04	98.93
2	.65	.19	< .04	n. d.	99.12	32	.04	.02	< .03	n. d.	99.91
4	.22	.06	< .04	n. d.	99.68	33	.06	.11	< .03	n. d.	99 80
5	.76	.36	< .03	n. d.	98.95	34	.13	.40	< .02	n. d.	99.45
6	.27	.07	< .03	n. d.	99.63	35	.29	.11	< .04	n. d.	99.56
7	.45	.12	< .04	n. d.	99.39	36	.38	.06	< .03	n. d.	99.53
8	.22	.26	< .04	n. d.	99.48	37	1.44	.06	< .02	n. d.	98.48
9	.42	.03	< .08	< .04	99.43	38	.20	.09	< .03	n. d.	99.68
11	.29	.05	< .07	< .06	99.53	39	.01	.01	< .03	n. d.	99.95
12	.28	.06	< .02	n. d.	99.64	41	.19	.11	< .03	n. d.	99.67
13	.60	.34	< .04	< .10	98.92	42	.44	.03	< .02	n. d.	99.51
14	.37	.09	< .02	n. d.	99.52	43	.03	.10	< .03	n. d.	99.84
15	.38	.03	< .03	n. d.	99.56	45	.01	.02	< .03	n. d.	99.94
16	.19	.02	< .03	n. d.	99.76	46	.04	.09	< .03	n. d.	99.84
17	.75	.20	< .03	n. d.	99.02	47	.33	.03	< .05	n. d.	99.59
18	.25	.11	< .04	n. d.	99.60	48	n. d.	.02	< .02	n. d.	99.96
19	.39	.12	< .04	n. d.	99.45	49	.08	.09	< .03	n. d.	99.80
20	.82	.06	< .03	n. d.	99.09	50	.09	.05	< .03	n. d.	99.83
21	.76	.22	< .03	n. d.	98.99	51	.18	.12	< .03	n. d.	99.67
22	1.14	.14	< .05	n. d.	98.67	53	.46	.25	< .03	n. d.	99.26
23	.39	.08	< .04	n. d.	99.49	54	.04	.03	< .02	n. d.	99.91
24	1.91	.09	< .04	n. d.	97.96	55	.03	.02	< .02	n. d.	99.93
26	.71	.23	< .03	n. d.	99.03	56	.36	.15	< .02	n. d.	99.47
28	.85	.19	< .05	n. d.	98.91	57	.19	.12	< .02	n. d.	99.67
29	.25	.03	< .05	n. d.	99.67	58	.12	.10	< .03	n. d.	99.75

TABLE 3.—*Composition of tin from filling after test of plugs that functioned*—Contd.

[n. d.=not detected]

Plug No.	Chemical composition					Plug No.	Chemical composition				
	Cu	Pb	Fe	Zn	Sn (by difference)		Cu	Pb	Fe	Zn	Sn (by difference)
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*		*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
59	0.80	1.10	<0.06	n. d.	98.04	81	0.47	0.18	<0.03	n. d.	99.32
60	.32	.09	<.02	n. d.	99.57	83	.37	.12	<.07	n. d.	99.44
61	.06	.16	<.05	n. d.	99.73	84	.17	.02	<.05	n. d.	99.76
62	.15	.04	<.01	n. d.	99.80	85	.69	.25	<.07	n. d.	98.99
63	.25	.09	<.03	n. d.	99.63	86	.14	.05	<.03	n. d.	99.78
64	.37	.07	<.04	n. d.	99.52	87	.05	.02	<.03	n. d.	99.90
66	.24	.07	<.01	n. d.	99.68	88	.22	.04	<.02	n. d.	99.72
67	.51	.17	<.02	n. d.	99.30	89	.50	.19	<.09	n. d.	99.22
68	.35	.17	<.02	n. d.	99.46	90	.25	.03	<.02	n. d.	99.70
69	.24	.06	<.01	n. d.	99.69	93	.90	.09	<.02	n. d.	98.99
70	.05	.03	<.03	n. d.	99.89	94	.14	.05	<.02	n. d.	99.79
71	.13	.21	<.05	n. d.	99.61	95	.10	.05	<.02	n. d.	99.83
72	.55	.11	<.06	n. d.	99.28	96	.26	.04	<.02	n. d.	99.68
73	.20	.15	<.03	n. d.	99.62	97	.93	.18	<.02	n. d.	98.87
74	.40	.05	<.03	n. d.	99.52	98	.27	.04	<.02	n. d.	99.67
75	.48	.10	<.04	n. d.	99.38	99	.18	.04	<.02	n. d.	99.76
77	.01	.02	<.03	n. d.	99.94	100	.22	.03	<.02	n. d.	99.73
78	.18	.27	<.04	n. d.	99.51	101	.36	.04	<.02	n. d.	99.58

It is of interest to note that of the total of 18 plugs that failed to function in the tests 15 were outside plugs and only 3 inside plugs, a ratio of 5 to 1. The ratio of outside to inside type of plug of all of the 150 plugs tested was less than 3 to 1, thus indicating that the inside type of plug is less liable to deterioration from the formation of the infusible crust. This may be due to the fact that the length of the inside type of plug is, in general, less than the length of the outside type, and in service the projection of the inside type of plug beyond the boiler shell into the fire chamber is less. Consequently, there is less danger of the tin melting and permitting the formation of the crust, as described later. These data are rather too few to allow drawing any general conclusions, but they indicate the desirability of having in all plugs the least possible length of projection of the fire end beyond the boiler shell into the fire chamber.

Chemical analyses of the infusible crusts indicated that they were chiefly stannic oxide (melting point 1,127° C.) with oxides of other metals present and in some instances a surprisingly large percentage of calcium sulphate (melting point 1,360° C.). As previously mentioned, in many of the plugs removed from service the tin had been melted out of the fire end. In cases where no crust was formed, the plug functioned properly. In other cases the tin or part of it was replaced by the dangerous oxides noted.

The general rules and regulations of the Steamboat Inspection Service require that "fusible plugs shall be so fitted that the smaller end of the filling is exposed to the fire and shall be at least 1 inch higher on the water side than the plate or flue in which they are fitted." Under these conditions it would be expected that any

TABLE 4.—*Classification of plugs that functioned and that did not function according to steamer boiler pressure*

BLEW OUT AT OR BELOW MELTING POINT OF TIN UNDER STEAM PRESSURE

[Steamer boiler pressures—pounds per square inch]

70 or less	80	100	110	120	125	130	140		150	155	170	180	190		200		210	215	220 and greater		Unknown pressure
9	64	134	57	60	14	71	32	11	84	16	33	43	13	74	2	17	100	70	4	22	1
10	67	108	62		15	72	87	12	89	36	34	45	20	75	66	18	101		5	23	30
59	69				94	77	115	38	93	40	35	46	27	126	85	19	117		6	24	95
63					107	78	116	39	105	47	37	50	28	127	86	26	118		7	62	109
135					110			56	106		41	55	29	129		49	119		8	139	138
136								58	159		42	88	61	130		81	120		21		140
								83	161		48	111	65	131		96	121				165
											51	137	68	132		97	122				168
											53	155	73	133		98	123				170
											54	156				99	124				
																	125				
TOTAL THAT FUNCTIONED																					
6	3	2	2	1	5	4	4		14	4	10	10	18		4		21	1	11		9
FAILED TO BLOW WHEN HEATED TO MELTING POINT OF TIN UNDER STEAM PRESSURE																					
109							91		103	102		44	31				25		3		
									104			52	76				79				
									92			112	128				80				
												154					82				
TOTAL THAT DID NOT FUNCTION																					
1							1		3	1		4	3				4		1		

molten tin in the fire end of the plug would run out. This occurs in the majority of cases. In fact, it is probable that the tin filling is melted out of the fire end after very few days or hours of service.

If the tin should not run out but remain in the plug in a molten condition, it probably would rapidly pick up copper from the casing and also might readily oxidize and finally fill up the fire end with the "infusible crust" noted. In order to determine the validity of this hypothesis, one end of a fusible plug was closed with a copper plug. A heating coil was wound around the casing and the entire plug heated to a temperature above the melting point of tin for approximately three months. The tin filling was left open to the air and was stirred about once a day with a glass rod. It was apparent that the tin was oxidizing and a hard infusible crust similar in appearance to that found in used plugs eventually formed. The appearance of the crust formed is shown in Figure 7 (*a*). A longitudinal section of the plug is shown in Figure 7 (*b*). It is evident that particles of the oxide had been stirred into the molten tin, and in time the oxide would have completely replaced the pure tin at least at this end of the plug.

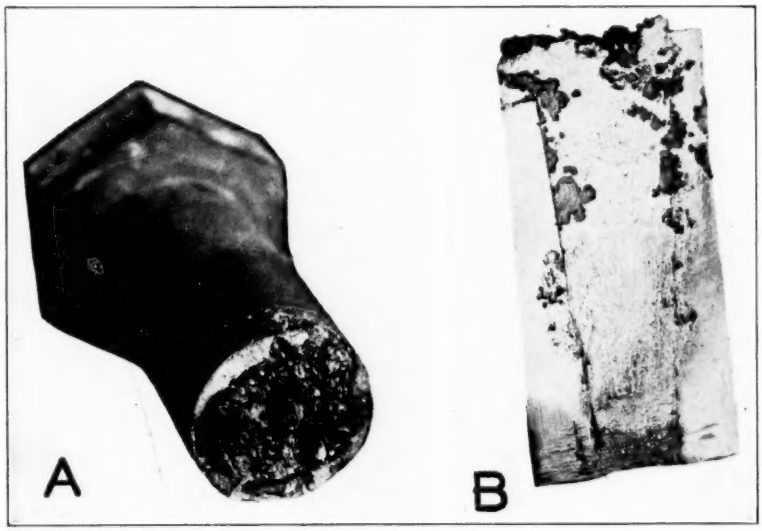

FIGURE 7.—*Infusible crust produced in plug in laboratory*

A, Shows oxide crust in end of filling; *B*, longitudinal section through filling.

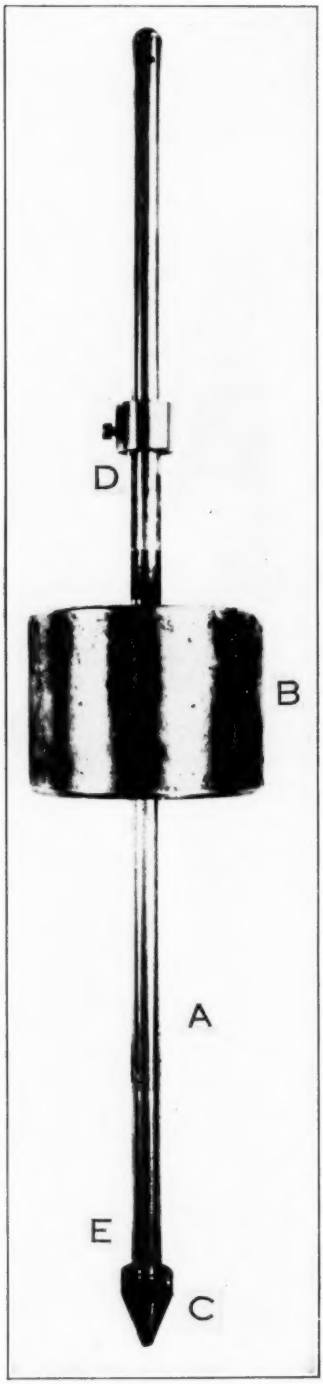

FIGURE 8.—*Device for testing tightness of filling*

The composition of this crust and filling was found to be as follows:

Crust.—Copper, 5.8 per cent; lead, 0.1 per cent; iron, 0.05 per cent; zinc, 0.10 per cent; SnO_2, remainder.

Filling.—Copper, 48.2 per cent; lead, 0.8 per cent; iron, 0.05 per cent; zinc, not detected; tin remainder.

It will be noted that the copper content of the tin has attained a very high value with a consequent raising of the melting point of the filling to approximately 650° C., considerably above that of pure tin. This, of course, is a very extreme condition, but emphasizes the importance of preventing molten tin from remaining in the plug.

An analysis was also made of the casing, which was found to have the following composition: Copper, 83.1 per cent; lead, 4.1 per cent; iron, 0.05 per cent; zinc, 6.8 per cent, and tin, 5 per cent; Ni, 0.20 per cent.

It is of interest to note that no zinc was found in the tin. Probably zinc was taken up by the tin while molten from the casing but was rapidly oxidized and so passed into the crust.

The validity of the theory of the formation of the crust is further confirmed by the statement of Inspector Hunter (letter of March 4, 1927, to the Supervising Inspector General, Steamboat Inspection Service) based on personal observation in service that it sometimes happens that "the tin does melt on the fire end and does run down, but does not entirely run out." He believes that this happens "more often in boilers operated under a high pressure forced draft." The reason for the tin not running out is the presence of obstructions, such as ash deposited in the plug in service after a small amount of the tin has melted and run out. Andrews, in a discussion of a paper by Warner,[3] has pointed out the necessity of frequent cleaning of fusible plugs to insure their proper operation.

In this investigation several plugs that failed to function had an appreciable percentage of calcium sulphate in the fire end intimately mixed with the oxides. The fact that the $CaSO_4$ was intimately mixed with the oxides indicated that it could not have been placed there as a filling to stop up a leak but probably was deposited gradually from the water in the boiler during service.

Plug No. 25 offers an explanation. A longitudinal section is shown in Figure 5. Examination indicated that the tin filling of this plug was not in intimate contact with the casing at all points, and a thin layer of $CaSO_4$ was found between the casing and the filling. Apparently the filling was not tight when placed in service or for some reason became slightly loosened in service and a slow leak developed. Calcium sulphate is one of the chief constituents of hard waters. It is readily conceivable that as the water leaked through the filling and reached the fire end of the boiler it evaporated and left a small deposit of the salts contained in the boiler water. Although the actual quantity of $CaSO_4$ in water is small, the total amount carried through the plug and deposited in the fire end could become sufficient to build up the crust noted over the period of 10 months that this plug was in service.

A confirmation of the possibility of this transfer of a salt from the boiler water to the fire end of a plug was given by plug No. 112. This plug when returned from service had a similar appearing deposit of scale on both the water end and the fire end. A sample of this scale

[3] Andrews, E., Some Causes for the Failure of Fusible Plugs, Power, **69**, p. 65; Jan. 8, 1929.

was scraped from the outside of the casing near the water end and the composition was found to be as follows: CaO, 8.4 per cent; MgO, 10.4 per cent; $Fe_2O_3(Al_2O_3)$, 2 per cent; Cu, 6 per cent; SO_3, 18.4 per cent; CO_2, present; insoluble matter, present.

It will be noted (Table 2) that the "infusible crust" in the fire end contained appreciable amounts of CaO and MgO. Apparently water leaked through the plug, and on evaporation at the fire end left the deposit of CaO and MgO, which became intimately mixed with the oxidized tin and copper. In fact, the presence of water or water vapor at the fire end may accelerate the oxidation. The conclusion is obvious that a plug showing any indications of a leak should be removed from service.

The present specifications for fusible plugs do not require any definite composition for the casings. Gurevitch and Hromatko [4] recommended that only a bronze with little or no zinc should be used for the casing material in order to avoid the possibility of contamination of the tin with zinc. In order to determine what is being used at the present time, chemical analyses were made of 31 of the casings returned from service. The results are given in Table 5. It appears that the recommendations as to use of a low zinc bronze casing is, in general, being followed.

TABLE 5.—*Composition of casings of plugs returned from service*

Plug No.	Chemical composition			
	Cu	Sn	Pb	Zn
	Per cent	*Per cent*	*Per cent*	*Per cent*
44 *	85.8	7.0	1.8	5.36
90	85.3	7.6	1.9	5.06
82 *	87.5	4.6	4.8	2.99
79 *	85.6	5.2	7.0	2.12
80 *	87.5	4.7	4.8	2.89
24	86.4	7.7	2.0	3.76
31 *	87.6	7.6	1.8	2.95
32	83.5	6.1	2.2	8.15
25 *	86.4	7.6	1.8	4.15
40	82.1	7.0	3.2	7.65
48	90.0	5.6	3.8	.55
3 *	86.0	6.7	1.3	5.94
53	87.5	6.9	5.0	.47
27	86.0	6.4	1.8	4.75
68	84.9	2.5	4.9	7.45
55	87.3	6.2	2.7	3.74
88	86.4	10.3	2.8	.45
93	85.3	2.0	4.3	8.15
96	87.3	6.7	1.2	4.75
87	85.1	9.6	4.9	.35
98	87.1	6.5	1.8	4.55
99	85.6	7.1	1.6	5.65
100	87.1	6.8	1.1	4.90
101	86.4	7.3	1.4	4.80
102 *	83.7	3.8	4.7	7.50
103 *	84.7	3.7	4.9	6.38
104 *	84.8	4.8	6.4	3.7
95	82.0	4.5	4.9	7.0
92 *	81.2	3.0	7.5	8.07
94	85.1	3.9	4.4	6.28
Average	84.95	5.89	3.48	4.30
Minimum	81.2	2.0	1.1	.35
Maximum	90.0	10.3	7.5	8.15

* Plug did not function in test after service.

[4] See footnote 2, p. 2.

There is no apparent reason why a rigid specification for the composition of the casing should be set except possibly a maximum zinc content. No data are available regarding the maximum zinc content that might be present and not contaminate the tin in service. There is no apparent relation between the zinc content of the casing and the failure of the plug to function as evidenced by the data in Table 5. Plugs having a casing with a low zinc content (No. 31), and also with a relatively high zinc content (No. 92) both failed to function in the "blow-out" test for reasons previously stated. On page 16 data are given which show that tin in a casing containing 6.8 per cent zinc, even when kept molten in the casing for three months, does not show an increase in zinc content, such zinc as it may pick up being rapidly oxidized and so passed into the crust.

It is evident that casings having a composition within the limits shown in Table 5 are satisfactory.

IV. SUMMARY

A series of tests has been carried out to determine the reliability of fusible plugs after about six months to one year of service. Special apparatus was devised with which it was possible to test fusible plugs under known steam pressures and temperatures simulating service conditions.

A total of 184 plugs which had been removed from service in various types of steam vessels were examined and 150 of them tested. Approximately 10 per cent of all plugs examined did not function when heated under steam pressure to the melting point of tin. The average length of service of these plugs was 10 months. One plug removed after only 2 months' service failed to operate. All other plugs tested that did not function had been in service at least 8 months. The maximum length of service permitted by the Steamboat Inspection Service is 18 months.

The plugs were removed from vessels of various types with low and high pressure boilers, coal and oil fired, and were made by several different manufacturers. They were, therefore, quite representative of the condition of all plugs in service.

While the total number of plugs tested was small relative to the total number in service, their representative character indicates that the same percentage of those that failed in tests in the laboratory would fail to function in service—namely, about 10 per cent. However, it should be noted that the regulations of the Steamboat Inspection Service require, in general, that at least two plugs shall be installed in all boilers under their jurisdiction. This appears to be a desirable precaution, since the probability of both plugs failing to function would be very small.

The cause of failure of the plugs to function was found in every case to be due to the presence in the fire end of a so-called "infusible crust" which had replaced the pure tin originally present. Chemical analysis showed this "infusible crust" to be chiefly stannic oxide intimately mixed with oxides and sulphates of copper and lead. In some instances an appreciable quantity of calcium sulphate was present and in one instance a small amount of magnesium carbonate or sulphate.

The formation of the "infusible crust" in some cases was believed to be due to the melting of the tin in the fire end and its being prevented from dropping out due to the presence of ash or other obstructions. The tin then apparently oxidizes, together with some of the copper from the casing, eventually replacing the tin in the fire end with a hard mass of very high melting point. In other instances the formation of the crust was found to be due to a small leak in the plug, permitting boiler water which may contain appreciable amounts of calcium and magnesium sulphates and carbonates reaching the fire end. Here it would be evaporated but leave a small deposit of the dissolved salts. Over a long period of time these deposits apparently become appreciable and eventually form a hard compact mass in the fire end.

The danger of the presence of an obstructing material forming in a plug during service which might prevent its functioning is evident.

V. GENERAL CONSIDERATIONS AND RECOMMENDATIONS

As a result of this investigation it was established that an appreciably large number, possibly 10 per cent, of plugs in service may have deteriorated after six or more months' service in such a manner that they probably would not function if called upon to do so.

The deterioration is the gradual development of a hard "infusible crust" in the fire end replacing the tin. This infusible crust consists principally of oxides of tin and copper and ash. In some instances salts common to boiler waters were found in the fire end believed due to a small leak in the plug.

The presence of this crust in the fire end constitutes a potential source of danger because of the false sense of security offered by a supposedly reliable safety device. Every effort should be made to eliminate the causes.

Engineers responsible for boilers equipped with fusible plugs should inspect the fire end at every opportunity. If there is at any time any evidence of a leak, the plug should be immediately replaced. All foreign matter, such as oxides, scoria, or any matter other than the tin, should be immediately removed. Leaky plugs are probably due to lack of proper bonding of the tin filling to the bronze casing.

Ford, in his discussion of the paper by Gurevitch [5] and Hromatko, emphasized the necessity of pouring the tin into the casing at a temperature sufficiently low, such that the tin freezes in less than one-half minute, so as to prevent solution by the molten tin of copper from the casing. However, if the temperature of pouring is too low the tin does not stick to the casing. At intermediate temperatures the tin may become only partially bonded to the casing, but sufficiently so to pass unobserved and yet develop a small leak in service.

Gurevitch and Hromatko showed that copper decreases the melting point of the tin to a minimum of 227.1° C. at the eutectic composition of 1 per cent copper. With increasing copper content the melting point increases rapidly.

There is no evidence that the presence of up to 1 per cent of copper in tin causes or promotes any deterioration that might in any way prevent the proper functioning of the plug in service. The principal cause of loose fillings (leaky fillings) is too low a temperature of

[5] See footnote 2, p. 2.

pouring. A low pouring temperature is used to avoid contamination with copper. The present requirements of the Steamboat Inspection Service permit a maximum impurity content of 0.30 per cent which includes the lead and iron normally present in tin. The manufacturer is thus forced to pour at a low temperature in order to keep the copper within specification requirements and yet at a temperature sufficiently high to obtain tight fillings. By permitting a higher copper content in the specification requirements, a higher pouring temperature could be used and so insure tighter fillings less liable to leakage. The Bureau of Standards has accordingly recommended to the Steamboat Inspection Service that the permissible copper content be increased to 0.5 per cent and the total impurity content to 0.7 per cent; the maximum limits of lead and zinc to remain as at present at 0.1 per cent each.

Coincident with this recommendation it has been emphasized that requirements as to tightness of filling should be written into the specifications. A loose filling is often detected by striking it on the small end with a punch and hammer. If loose, the filling will slip partially, sometimes entirely, out of the casing. A plug having such a filling should be rejected and the entire heat suspected.

The punch and hammer test is rather indeterminate due to differences in weight of hammer and force of blow that may be used by different persons. To insure greater uniformity, the device shown in Figure 8 was developed and has been used quite satisfactorily in routine testing of plugs. It consists of a slide rod A and a 2-pound weight B. In testing the tightness of a filling the point C is placed against the small end of the tin filling and weight B permitted to drop through the distance d–e, of 6 inches. Three such blows will generally indicate whether the filling is loose by forcing it to slide partially out of the casing.

The present regulations of the Steamboat Inspection Service permit the small end of taper in a fusible plug to "be countersunk not more than one-fourth of an inch in depth and width." When such a countersink is present, the tin in that portion of the bore acts to prevent a filling, even if loose, from being driven out. It is believed, therefore, that this countersink should not be permitted.

The looseness or tightness of a filling is directly related to proper alloying of the tin filling with the casing. It is often noted in melting out fillings of plugs submitted for test for chemical analysis of the tin filling that the tin of the filling has not alloyed with the casing as evidenced by areas showing the bare surface of the casing. Obviously, the bore of a casing showing this condition was not properly cleaned or tinned before pouring in of the filling. It is believed that all plugs from any heat should be rejected in which a plug shows such evidence of lack of bonding of the tin with the casing.

The data are too few to support specific recommendations regarding modifications in design of plug. It appears desirable, however, that the projection of any plug beyond the boiler shell into the fire chamber should be a minimum. This should be readily obtainable in the inside type of plug by so fixing the position of the threads on the casing such that, when placing it in position, the fire end can be forced but a short distance beyond the outer surface of the boiler sheet. In the outside type of plug the relation of the position of the threads to the head (fire end) of casing should be designed such that in placing the plug

in position the head will go in as nearly flush with the outside surface of boiler sheet as possible.

VI. ACKNOWLEDGMENTS

The authors wish to express their appreciation for the indispensable cooperation and interest of the Steamboat Inspection Service and to R. D. France for valuable assistance in conducting the tests.

WASHINGTON, June 22, 1929.

A SIMPLE CONTROL STOPCOCK FOR GAS ANALYSIS APPARATUS

By Martin Shepherd

ABSTRACT

This note describes a simple control stopcock for gas analysis apparatus. The control permits pressure balance to be obtained easily, quickly, and with high accuracy. Diffusion errors are eliminated without danger of emptying the manometer. The accidental surge of pipette reagents into the train is prevented. Difficult combustions of heavy hydrocarbons may be made without the deposition of carbon. The technique of operation and actual means of construction of the stopcock are described.

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I. A TECHNIQUE FOR OBTAINING PRESSURE BALANCE IN GAS ANALYSIS UNITS

The technique usually employed to obtain a pressure balance in the ordinary gas analysis apparatus consists of a vertical movement of the levelling bulb which supplies the confining fluid to the burette. This adjustment is made by hand or by some gear system. The first is inaccurate and the second cumbersome.

A simple and accurate technique, which has been used for many years at the Bureau of Standards, may be described with reference to the assembly drawing of the gas-analysis unit shown in Figure 1. The levelling bulb *L* is connected to the burette *B* through the stopcock *3*. The pressure balance is obtained simultaneously within the burette and distributing train *T* by adjusting the tee cock *1* to connect the train on both sides with the manometer *M* interposed between the burette and the compensator *C*. The correct pressure balance is indicated in *M* by a platinum point placed in the arm adjacent to the compensator. When a rising mercury meniscus makes contact with this point, an electric circuit is closed, lighting a 2-volt lamp. This assembly and method of indicating the point of balance are well known and have been previously described.

Pressure balance in such a unit may be easily adjusted as follows: With stopcock *2* closed and stopcock *3* opened, the pressure in the burette is roughly adjusted to about 1 cm less than atmospheric with the levelling bulb held in the hand. This will prevent emptying the mercury from the manometer. The leveling bulb is then placed on the split ring *R* and the stopcock *3* is slowly opened to permit the entrance of the confining fluid to the burette, which gradually increases the pressure until the manometer indicates this to be equal to the pressure within the compensator. Stopcock *3* is instantly closed and the burette reading may be taken.

The only objection offered to this method lies in the difficulty of only slightly opening the lower burette cock. This must be opened

very slowly, and the operation is somewhat troublesome to master. It is frequently necessary to repeat the operation several times before a successful adjustment is attained. A further complication may arise from the presence of a slight excess of lubricant around the bore or outlet of the cock, which oftens dams the flow of the confining fluid until the cock has been opened too far.

II. THE CONTROL STOPCOCK

The stopcock shown in Figure 2 completely eliminates such difficulties. The plug of this cock has two bores, one of which has the fine constriction shown. Rough adjustments may be made through the open bore, following which a 90° turn of the plug admits an extremely slow flow of mercury to the burette. The mercury can be quickly raised to within a millimeter from the contact point of the manometer by partially opening the full bore. A turn of the key through 90° opens the constricted bore and completes the contact, the mercury rising so slowly that the eye is unable to determine when contact has been made until the lamp reveals it.

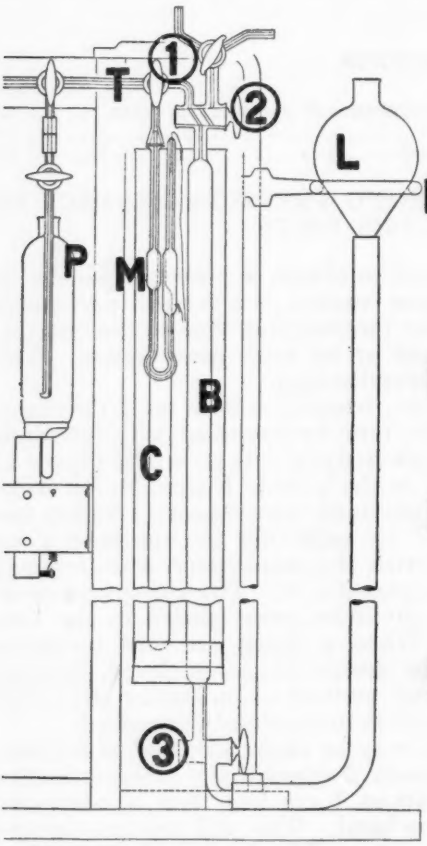

FIGURE 1.—*Partial assembly of gas analysis unit*

Three additional split rings, R_2 whose positions are at the points R_1, R_2, and R_3, indicated in Figure 1 are placed at even intervals. The position of the lower ring is such that when the leveling bulb R_3 is resting thereon and stopcock *3* is opened the mercury level within the burette stands just below the 100 ml etch mark. Such an arrangement permits the operator to maintain a roughly equal head of mercury on the burette when making pressure adjustments. This will cause a fairly uniform rate of flow of mercury in the manometer toward the contact point, a result which is quite desirable. The time lag in closing cock *3* after contact has been made results in no measureable error whatsoever, because of the uniform and very slow rate of flow of the manometer mercury.

The precision with which pressure balance can be obtained by this method is only one of the advantages accruing from the use of

the control cock. There are several other benefits which should be considered.

It is desirable to displace the gas confined in the manometer arm connected to the distributing train before passage to any of the pipettes of the apparatus. Any part of the gas sample which has diffused into this arm of the manometer may be drawn into the burette by placing the leveling bulb on the lower split ring and opening stopcock *3*. The thread of mercury in the capillary lead to stopcock *1* can be safely controlled by using the constricted bore of the control cock. There is thus no danger of emptying the manometer mercury into the train.

Check valves placed in the capillaries leading from the absorption pipettes to the train have been found to be generally unsatisfactory. When no automatic check is provided there is ever present the possibility of drawing a reagent from the pipettes into the train. The control cock eliminates this danger and makes it possible to accurately bring the reagent from the pipette to an etch mark on the capillary lead. Furthermore, if one of the bubbling types of pipette

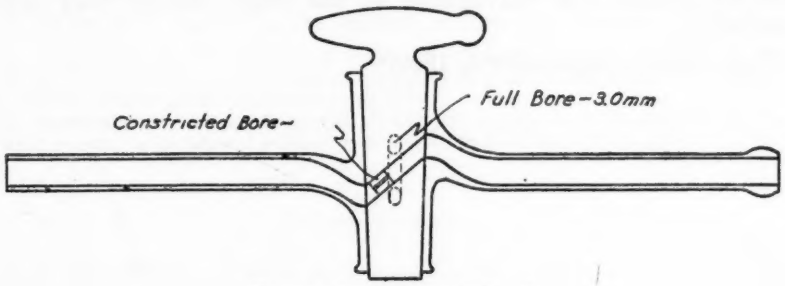

FIGURE 2.—*The control cock*

is used, it occasionally happens that the diagonal bore of its stopcock may become temporarily plugged with lubricant. When this occurs the reagent is instantly drawn into the train through the capillary inlet of the pipette, even though the stopcock is turned to the correct position to withdraw gas from the pipette. To prevent such an accident the control cock may be turned to the constricted bore when first the gas is to be withdrawn. If the reagent does not slowly rise in the capillary inlet of the pipette, the cock may be immediately opened to the full bore.

It is difficult to obtain a quantitative combustion of acetylene, ethylene, ethane, propane, and heavy hydrocarbons in an atmosphere of oxygen over a heated platinum spiral. Unless the rate of flow of the hydrocarbon into the combustion pipette is very slow, deposition of carbon occurs. During some recent analyses of propane-ethane mixtures it was found impossible to prevent the deposition of carbon unless the gas was admitted at the slow rate insured by use of the control cock.

III. CONSTRUCTION OF THE CONTROL STOPCOCK

This stopcock may be made in several ways. The glass blower may seal a No. 38 (B. and S. gage) copper wire into the solid key and along the axis of one bore. The key is then drilled out from opposite

sides, leaving an undrilled portion of 2 to 3 mm thickness just off the center of the key. Nitric acid is used to remove the copper wire remaining in the undrilled portion.

Another method is as follows: Draw down an ordinary 7-mm glass tube so that one end is sealed shut and the outside diameter of the drawn-out portion of the tube snugly fits the ordinary 3 or 4 mm bore of the stopcock. Cut 2 or 3 mm segments from this tube beginning at the point where the tube first opens to a fine capillary. Select a segment of the proper bore and cement this within the ordinary bore of the stopcock plug. DeKotinsky cement has been found suitable for this purpose.

It is evident that the fine constriction must be placed away from the outside surface of the stopcock plug. When this is done no trouble results from plugging by the stopcock lubricant.

A possible modification of the control cock would be to provide the burette with two lower stopcocks terminating at both ends in a Y junction. A section of very fine capillary tubing could then be sealed into the lead of one stopcock. Such an arrangement, however, does not possess the convenience of the single control cock here described.

WASHINGTON, September 4, 1929.

THROWING POWER IN CHROMIUM PLATING

By H. L. Farber[1] and W. Blum

ABSTRACT

During recent years chromium plating has come into extensive use in spite of the fact that it is very difficult to deposit chromium in recesses of irregularly shaped articles. General principles show that in the chromic acid baths used for plating there is little hope of radically improving the "throwing power." The purpose of this investigation was to define those operating conditions which yield the highest throwing power, which at best is poor.

The ratio of the weights of metal deposited on two cathodes, one of which is twice as far from a gauze anode as the other, gives a quantitative measure of throwing power. If, under these conditions, as is invariably true in chromium plating, this metal ratio is greater than 2 : 1, the throwing power is negative. The best throwing power obtained was −13 per cent. Under less favorable conditions it was −100 per cent or still poorer.

The conditions found to yield the best throwing power are (*a*) a high temperature such as 55° C. (131° F.); (*b*) a high current density such as 35 amp./dm.^{2} (325 amp./ft.^{2}); (*c*) a low concentration of chromic acid such as 150 to 250 g/L (20 to 33 oz./gal.); and (*d*) a low sulphate content, for example, $\frac{CrO_3}{SO_4}=200$. These conditions usually require a potential of over 6 volts. If this is not available, fair throwing power can be obtained in a more concentrated solution with a lower temperature and current density.

The numerical results for throwing power are approximately parallel to the covering power, as measured with copper cathodes bent at right angles.

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[1] Research associate of the American Electroplaters' Society. During the past few years, this society, composed chiefly of foreman platers, has collected a research fund from its members and from firms engaged in electroplating. This fund is used to pay the salaries and traveling expenses of research associates engaged at the Bureau of Standards in investigations upon plating problems. This paper presents the results obtained in one of these researches.

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I. INTRODUCTION

In recent years chromium plating has come into very extensive use, especially upon such articles as automobile and plumbing fixtures, where appearance and resistance to tarnish and abrasion are important. One of the greatest difficulties in chromium plating is the poor throwing power, which makes it hard to deposit chromium in the recesses of irregularly shaped articles. No marked improvements in throwing power have been brought about in recent years, and the present commercial success in chromium plating is due more to the ingenuity of the platers than to the use of any new principles or discoveries.

The published researches on the behavior of the chromic acid baths now used for chromium plating show that there is little hope of making radical improvements in their throwing power. It was believed however that a systematic study of all the factors involved would probably permit the selection of conditions which would at least yield somewhat more uniform metal distribution than is commonly obtained. As will be shown, this prediction has been justified.

II. HISTORICAL

Although many papers have been published upon chromium plating, in some of which the throwing power is referred to or discussed, very few specific researches have been published on this subject. H. E. Haring and W. P. Barrows [2] reported no actual measurements of throwing power, but from a consideration of the factors involved, they concluded that "it is doubtful whether the throwing power of the chromic acid plating bath can be decidedly improved by the necessarily limited changes which can be made in its composition." They then predicted that the most favorable conditions for good throwing power would be (1) a relatively low concentration of chromic acid; (2) relatively high temperature and current density; (3) deposition on a metal of high hydrogen overvoltage, such as copper; (4) closing the circuit by the introduction of the cathode; and (5) using a reverse current on iron or steel for a few minutes.

R. Schneidewind in a comprehensive summary of his own and other researches on chromium plating [3] made little distinction between the throwing power and the bright plating range which, as will be explained, are closely related to each other, but by no means identical.

[2] B. S. Tech. Paper No. 346; 1927. [3] Univ. Michigan Eng. Res. Bull. No. 10; 1928.

Most of his qualitative conclusions regarding throwing power apparently referred more to the range of bright deposits than to the relative thicknesses of the deposits, which latter factor determines the throwing power as quantitatively defined. While it is possible to derive definite values of throwing power from Schneidewind's data on cathode efficiencies, no such quantitative conclusions were drawn by that author.

O. J. Sizelove [4] employed cathodes bent at right angles to measure the relative throwing powers under different conditions. He found that a low sulphate content and a high current density are favorable for good throwing power.

W. L. Pinner and E. M. Baker [5] also used bent cathodes to measure the throwing power and thus defined the optimum ratio of chromic acid to sulphate in the baths.

In addition to the above publications, many other papers include discussions of or qualitative references to the throwing power of chromic acid solutions, but so far as known, no quantitative values of the throwing power have been published.

III. PRINCIPLES INVOLVED

1. THROWING POWER

(a) DEFINITIONS

While it is readily possible to make qualitative observations upon throwing power by plating recessed articles, such as bent cathodes or other irregular shapes, it is not feasible to express such results upon a numerical basis that is suitable for quantitative comparisons. The definition of and method of measuring throwing power that will be used in this paper are those which were described in previous papers from this bureau.[6] These principles may be summarized as follows:

Upon any irregularly shaped cathode there is a certain "primary current distribution," determined solely by the shapes and relative positions of the cathode, the anode, and the container. This current distribution is that which is produced when there is no cathode polarization, for example, when an alternating current of sufficiently high frequency is used. It is independent of the composition or properties of the plating solution. If a far part F of a cathode is five times as far from the anode as a near part N (and hence the resistance from the anode to F is five times that to N) the primary current density on the far part will be only one-fifth that on the near part. If this primary current distribution prevails, and if the efficiency of deposition is the same at the two current densities, the "metal distribution" on these two points will also be 5:1, and the metal coating will be five times as thick on the near as on the far part.

If, however, by some property of the solution or of the plating process the metal ratio is made 4:1 instead of 5:1, the article is more uniformly plated, and there is a positive "throwing power." This is defined as the improvement, in per cent, of the metal distribution ratio above the primary current ratio. If the metal distribution ratio

[4] Monthly Rev. Am. Electroplaters' Soc., **16**, April, 1929.
[5] Trans. Am. Electrochem. Soc., **55**, preprint; 1929.
[6] H. E. Haring and W. Blum, Current Distribution and Throwing Power in Electrodeposition, Trans. Am. Electrochem. Soc., **44**, p. 313; 1923. H. E. Haring, Throwing Power, Cathode Potentials and Efficiencies in Nickel Deposition, Trans. Am. Electrochem. Soc., **46**, p. 107; 1924.

is 4:1 and the primary ratio is 5:1, the throwing power is $\frac{5-4}{5}=\frac{1}{5}=+20$ per cent. If in another case the metal ratio is 6:1 instead of 5:1, the metal is less uniformly distributed than corresponds to the shape and position of the article. The throwing power is then negative, and is equal to $\frac{5-6}{5}=-\frac{1}{5}=-20$ per cent. As will be shown, the throwing power in the present chromic acid baths is invariably negative, and the best that can be hoped is to make it less negative. Thus a throwing power of -25 per cent is better than one of -100 per cent, even though both are negative, and poor compared with the throwing power in nickel and copper deposition.

In order to measure the throwing power, all that is necessary is a rectangular box in which a perforated anode and two plane cathodes (connected together) are placed at definite distances, so that they completely fill the cross section of the solution. Of these plates N represents a near point on the cathode and F a far point. By weighing these cathodes before and after plating the weights of deposits on the two are determined. From these weights and the relative distances from the anode the throwing power is easily calculated.

Thus, if the plates are, respectively, 5 and 10 cm (2 and 4 inches) from the anode, the primary ratio is 2:1. If then the metal deposit on the near plate weighs 0.637 g and on the far plate 0.232 g, the metal ratio is $\frac{0.637}{0.232}=2.74$. The throwing power is therefore.

$$\frac{2-2.74}{2.0}=-\frac{0.74}{2}=-0.37=-37 \text{ per cent}$$

The numerical values obtained for throwing power depend upon the size and shape of the throwing-power box and the primary ratio employed. While the data obtained in a given apparatus are comparable with each other, they are not directly comparable with those obtained in a different apparatus. For uniformity it is suggested that the box (or rather the solution) have a cross section of 5 by 5 cm (2 by 2 inches) and a distance between cathodes of 15 cm (6 inches)[7] For most plating solutions a primary ratio of 5:1 is satisfactory, but for chromium plating a ratio of 2:1 is preferable because satisfactory deposits can seldom be obtained with a current ratio as great as 5:1. All published results for throwing power should include a statement of the primary ratio.

(b) FACTORS INVOLVED

It has been shown by Haring and Blum [8] that the throwing power depends only upon three factors, viz, (1) cathode polarization, (2) conductivity, and (3) cathode efficiency. Their effects may be summarized as follows, with special reference to chromium plating.

(1) *Cathode polarization.*—When any metal is deposited upon a cathode, the concentration of metal in the adjacent solution (the cathode film) decreases, and hence a higher potential is required to cause metal deposition than from the original concentration. This increase in potential is called the cathode polarization. In general,

[7] Such an apparatus, which is useful also for measuring polarization and conductivity is now available from the State Manufacturing Co., of Chicago, Ill.

[8] See footnote 6, p. 29.

it increases as the current density is increased. Typical cathode and anode polarization curves for chromium deposition are shown in Figure 1, reprinted from Bureau of Standards Technologic Paper No. 346.

As shown in Figure 2 (from B. S. Tech. Paper No. 346) the total voltage drop between the anode and cathode in any electrolysis is the sum of (1) the decomposition potential; (2) the *IR* drop, which is the product of the current *I* and resistance *R;* (3) the anode polarization; and (4) the cathode polarization. For simplicity we may consider that in a given operation (1) and (3) are constant. Then the rest of the voltage is equal to the *IR* drop plus the cathode polarization. The total voltage between the anode and the near and far parts of the cathode, respectively, is the same if the anode and

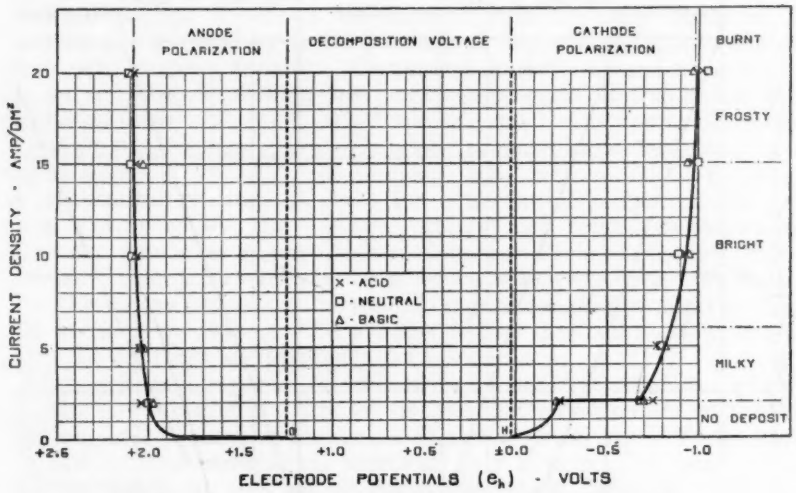

FIGURE 1.—*Electrode potentials in chromium deposition*

CrO_3—250 g/L; SO_4—0.25 g/L; 45° C.; lead anode; steel cathode.

cathode are good conductors. Any increase in cathode polarization due to the higher current density on the near point will necessarily result in a lower *IR* drop to that point. As for a given solution, the resistance to the near point is fixed, the current *I* and, hence, the current density on the near point must decrease and become more nearly equal to that on the far point. This tendency to equalize the current densities causes an increase in throwing power. In general, the throwing power is better when the cathode polarization increases greatly with an increase in current density.

Actually in chromium plating as shown in Figure 1, the cathode polarization increases very slightly with the current density within the range of bright deposits. Hence, there can be no appreciable positive throwing power in chromic acid solutions.

(2) *Conductivity.*—The conductivity (or resistivity) of the solution determines the *IR* drop through a certain path with a given current. By increasing the conductivity the value of *IR* is decreased. This increases the relative effect of any change in cathode polarization upon the throwing power. If, however, as in chromium plating, the

change in cathode polarization is small, the effect of an improvement in conductivity is also negligible. Any effect of conductivity is rendered still less significant by the fact that high current densities are used in chromium plating and, hence, the IR drop is high even when R is low. The conductivity of the chromic acid solution, therefore, has no appreciable effect on the throwing power.

(3) *Cathode efficiency.*—If the cathode efficiency increases as the current density is increased, this tends to make the metal coating relatively thicker at the near point, where the current density is high, than corresponds to the actual or "secondary" current distribution. This represents a decrease in throwing power, which

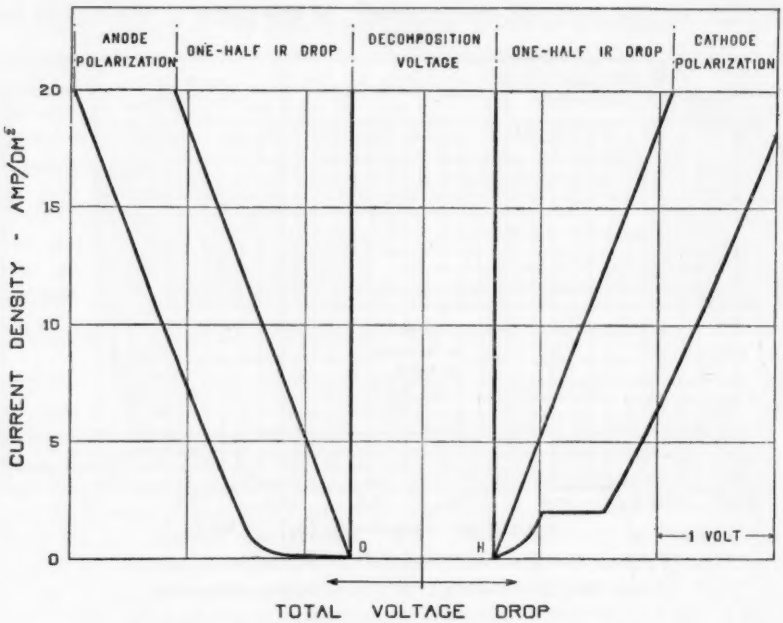

FIGURE 2.—*Total voltage used in chromium deposition*

CrO_3—250 g/L; SO_4—0.25 g/L; 45° C.; lead anode; steel cathode; 10 cm apart.

then may become negative. Suppose that, as a result of cathode polarization, the current densities on the near and far plates are in the ratio of 1.8:1 when the primary ratio is 2:1. This corresponds to a throwing power of +10 per cent if the cathode efficiencies are equal at the two current densities. But if, as is probable in chromium plating, the cathode efficiency is 15 per cent on the near plate and 10 per cent on the far plate, the actual weights (or thicknesses) of the metal on the two plates are in the ratio of

$$\frac{1.8}{1.0}\times\frac{15}{10}=\frac{2.7}{1.0}=2.7:1$$

and the throwing power is

$$\frac{2-2.7}{2.0}=-0.35=-35 \text{ per cent}$$

A negative throwing power is possible only if the cathode efficiency increases with the current density. This condition exists whenever, as in nickel and chromium deposition, it is easier to discharge hydrogen than metal. At some low current density only hydrogen will be liberated, but as the current density increases to a certain value, metal starts to deposit. Further increases in current density improve the cathode efficiency. This condition is the principal cause of the poor throwing power in chromium plating. Hence, the only hope of improving the throwing power is to employ those conditions under which the current efficiency is most nearly uniform for the maximum and minimum current densities. This investigation has resolved itself largely into a study of cathode efficiencies in chromium deposition.

2. PLATING RANGE

In all plating processes the crystal structure and luster of the deposits are affected by the conditions of deposition, such as temperature and current density. Chromium is not unusual except in so far as (*a*) the conditions for producing bright deposits are more restricted than with most other metals, and (*b*) as the hardness and difficulty of polishing chromium make it more important to produce bright deposits initially. In consequence, the conditions employed for chromium plating, at least for ornamental purposes, are fixed almost entirely by the "plating range" of bright deposits, and throwing power as above defined is generally a secondary factor. The chief concern usually is to produce a bright chromium coating over the entire surface to be plated, regardless of the relative thickness in the depressions. To a large degree this course is warranted when the coatings are primarily for appearance.

The range of temperature and current density within which bright deposits are obtainable can be determined experimentally for any solution, and plotted as shown in Figure 3 (from B. S. Tech. Paper No. 346). Such curves are, however, only approximate because it is hard to decide at the border lines just which deposits are bright, milky, frosty, or burnt.

3. COVERING POWER

The ability to completely cover a cathode, which may be referred to as the "covering power," is closely related to the throwing power as above defined, but is not so readily defined quantitatively. Strictly speaking, the covering power relates to the process or extent of covering the cathode, while the throwing power (as here defined) is an expression of the relative thicknesses of the deposits on two parts of the cathode after they are covered. As will be shown by the tests with bent cathodes, the covering power is practically parallel to the throwing power. The data for the latter are, however, more useful for quantitative comparisons.

IV. METHODS OF REGULATING THE PRIMARY CURRENT DISTRIBUTION

Research and experience have shown that, for a given solution and temperature, bright chromium deposits can be produced only between certain current densities, and that, in general, the covering power and throwing power are poor. It is obvious that if a cathode is of such

a shape, or can be so placed in the bath, that the current density is uniform over the entire surface, the difficulties of plating range, covering power, and throwing power will entirely disappear. Such a state exists only under ideal conditions which can seldom be obtained or maintained. It is possible, however, by proper ingenuity to obtain more nearly uniform current densities than exist under usual conditions, and thus largely overcome the above difficulties. It is rarely possible to plate completely with bright chromium any object on which the maximum current density is more than five times the minimum. For general work it is desirable to reduce this ratio to

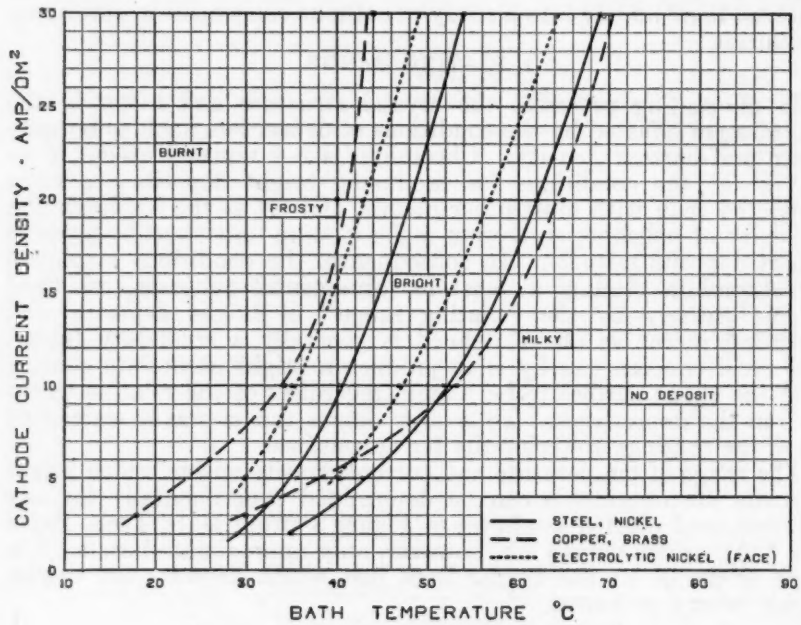

FIGURE 3.—*Plating range on different metals*

CrO_3—250 g/L; SO_4—0.25 g/L.

not more than 3 to 1. This can be accomplished (or approached) by four methods, all of which have long been used for other kinds of plating. They are especially useful for chromium plating.

1. USE OF CONCENTRIC OR PARALLEL ANODES AND CATHODES

When the cathodes are plane surfaces, the current density can be made almost exactly uniform by having parallel anodes, which, as well as the cathodes, completely fill the cross section of the solution. Cylindrical tubes can be plated uniformly by having anode rods inside them or cylindrical anodes surrounding them. The same principle is involved in the use of inside anodes of any kind, such as those used in plating parabolic lamp reflectors. Experience has shown that for such purposes exact parallelism is not necessary and may be undesirable. This is because of secondary effects due to unequal heating or circulation and to the passage of excess currents

to points and edges. In general, all such arrangements must be based on trial. They are not practicable when the articles are of very irregular shapes.

2. INCREASING THE DISTANCE BETWEEN THE ANODES AND CATHODES

When an article of irregular shape is relatively close to the anode, the near points receive much higher current densities than the far points in the depressions. By simply moving the articles farther from the anode the current densities are made more uniform. Suppose, for example, that a cup-shaped piece has a depth of 10 cm (4 inches) and is hung so that the edge is only 2.5 cm (1 inch) from the anode; then the current density on the edge will be at least five times as great as in the bottom. Actually the ratio will be much larger, owing to the tendency of projecting points or edges to receive an excessive current through the surrounding solution, and for the depression to be shielded so as to get comparatively few current lines. By moving the cathode so that the edge is 10 cm (4 inches) from the anode, the current density there will be only about twice that in the recess. By moving it still farther away the ratio will become still more nearly unity.

The practical objection to this procedure is that by increasing the average distance between the anodes and cathodes, the voltage necessary for securing a given current density must also be increased. This is especially objectionable if the available potential is not more than 6 volts. In that case the distance must be fixed by the maximum voltage. Actually in chromium plating this objection is not so serious as in other plating because (see fig. 2) the *IR* drop, the only factor affected by the distance, represents only a small part of the total voltage. Under most conditions an increase in average distance from 10 to 20 cm (4 to 8 inches) involves not more than 20 per cent increase in voltage; for example, an increase from 5 to 6 volts. This method of securing uniform current densities is especially adapted for plating small parts, as then even when the tank is "full" the anode area is usually larger than the cathode area, which relation reduces the necessary voltage (and is otherwise desirable). Practically, average distances of 20 to 30 cm (8 to 12 inches) are found advantageous.

3. USE OF ADJACENT CONDUCTORS

It has long been the practice of electroplaters, especially when producing thick metal deposits as in electroforming, to attach metal wires or rods to the cathodes, near those parts which otherwise tend to receive excessive current densities and "burnt" deposits. The wire serves to attract part of the current and, in the language of the old-time platers, acts as a "thief." This principle has been very successfully applied in chromium plating, especially of small parts having sharp projections on which a "burnt" deposit is likely to form. When these articles are hung on metal racks in such a way that the exposed points are adjacent to a metal rod which forms part of the rack, or to other parts of the cathodes, the current density is made more uniform on the articles, and complete plating can be accomplished without burning on the projections. In some cases a wire cage or basket is attached so as to surround the projecting points.

4. USE OF NONMETALLIC SHIELDS

Another way to prevent the current density from being excessive on the projecting portions of the cathode is to shield them by strips of insulating material such as glass, bakelite, or hard rubber. This method is the least convenient and is used only in extreme cases. One difficulty is that of obtaining insulating materials that are not attacked by the warm, strong chromic acid baths. When, as is now a frequent practice, wire-glass linings are used in the plating tanks, the hanging of articles so that projecting parts are near the side of the tank results in a shielding of this type.

V. METHODS OF STUDY

1. MATERIALS EMPLOYED

The chromic acid used in these tests was a high-grade commercial product furnished for electroplating. Analyses of this material showed that it contained 99.5 per cent CrO_3, 0.2 per cent Cr_2O_3, 0.08 per cent SO_4, and 0.20 per cent insoluble matter. As sulphate and trivalent chromium were present in much smaller concentrations than those to be added to most of the baths, no attempt was made to purify this chromic acid.

"Chemically pure" sulphuric acid was used to furnish the desired sulphate content, except in those few solutions in which other sulphates are designated. The latter were added in the form of analyzed stock solutions of "reagent chemicals," as was also the sodium dichromate used in a few baths.

Stock solutions of chromic acid with a high content of trivalent chromium, subsequently determined by analysis, were prepared by (*a*) electrolyzing chromic acid with platinum electrodes, and (*b*) dissolving in chromic acid dry chromium hydroxide, that contained a small amount of sulphate, which was determined and allowed for in the solutions prepared from this material. The results were identical with solutions of the same concentrations prepared by these two methods.

All chromium plating solutions were analyzed by the methods described in Bureau of Standards Technologic Paper No. 346. The compositions of the principal solutions used in this study are shown in Table 1.

TABLE 1.—*Composition of chromium-plating solutions*

Soln. No.	Chromic acid, CrO_3			Sulphate, SO_4			Weight Ratio $\frac{CrO_3}{SO_4}$	Name	Other constituents				Remarks
	M	g/L	oz./gal.	N	g/L	oz./gal.			Formula	N	g/L	oz./gal.	
1	1.5	150	20	0.03	1.5	0.20	100						
2	2.5	250	33	.05	2.5	.33	100						
3	4.0	400	53	.08	4.0	.53	100						
4	1.5	150	20	.015	.75	.10	200						
5	2.5	250	33	.025	1.25	.17	200						
6	4.0	400	53	.04	2.0	.27	200						
7	1.5	150	20	.06	3.0	.40	50						
8	2.5	250	33	.10	5.0	.67	50						
9	4.0	400	53	.16	8.0	1.07	50						
10	2.5	250	33	.05	2.5	.33	100	Sodium dichromate	$Na_2Cr_2O_7.2H_2O$	0.75*M*	224	30	
11	2.5	250	33	.025	1.25	.17	200						
12	2.5	250	33	.05	2.5	.33	100	Boric acid	H_3BO_3	.1*M*	6	.8	
13	2.5	250	33	.05	2.5	.33	100	do	do	.25*M*	15	2.0	
14	2.5	250	33	.05	2.5	.33	100	Trivalent chromium	Cr^{III}	.05	.87	.12	$Cr_2(SO_4)_3$.
15	2.5	250	33	.05	2.5	.33	100	do	do	.16	2.8	.38	Electrolytic.
16	2.5	250	33	.05	2.5	.33	100	do	do	.18	3.1	.42	$Cr(OH)_3$.
17	1.5	150	20	.03	1.5	.20	100	do	do	.50	8.7	1.2	Do.
18	2.5	250	33	.05	2.5	.33	100	do	do	.50	8.7	1.2	Do.
19	4.0	400	53	.08	4.0	.53	100	do	do	.50	8.7	1.2	Do.
20	2.5	250	33	.05	2.5	.33	100	do	do	1.0	17.3	2.3	Do.
21	2.5	250	33	.05	2.5	.33	100	do	do	2.0	34.6	4.6	Do.
22	2.5	250	33	.05	2.5	.33	100	do	do	2.5	43.3	5.8	Do.
23	4.0	400	53	.08	4.0	.53	100	do	do	.80	13.9	1.8	Do.
24	2.5	250	33	.025	1.25	.17	200	do	do	.50	8.7	1.2	Do.
25	2.5	250	33	.10	5.0	.67	50	do	do	.50	8.7	1.2	Do.
26	2.5	250	33	.05	2.5	.33	100	Iron	Fe^{III}	.20	3.7	.5	$Fe(OH)_3$.
27	2.5	250	33	.05	2.5	.33	100	do	do	.50	9.3	1.2	Do.
28	2.5	250	33	.05	2.5	.33	100	do	do	1.0	18.7	2.5	Do.
29	2.5	250	33	.05	2.5	.33	100	do	do	2.0	37.3	5.0	Do.
30	1.5	150	20	.03	1.5	.20	100	do	do	1.0	18.7	2.5	Do.
31	4.0	400	53	.08	4.0	.53	100	do	do	1.0	18.7	2.5	Do.
32	2.5	250	33	.025	1.25	.17	200	do	do	1.0	18.7	2.5	Do.
33	2.5	250	33	.10	5.0	.67	50	do	do	1.0	18.7	2.5	Do.
34	2.5	250	33	.05	2.5	.33	100	do	do	.50	9.3	1.2	Do.
								Trivalent chromium	Cr^{III}	.50	8.7	1.2	$Cr(OH)_3$.
35	2.5	250	33	.05	2.5	.33	100	do	do	.08	1.3	.17	Chromite.
								Iron	Fe^{III}	.05	.9	.12	

2. THROWING POWER AND CATHODE EFFICIENCY

It was found impracticable to use the regular hard-rubber throwing power box, as the rubber was slowly attacked by the chromic acid, with the simultaneous reduction of the latter to trivalent chromium. Attempts to have an accurately dimensioned glass box made in one piece have not thus far succeeded. A box made of plate glass with joints sealed with a mixture of powdered silica and sodium silicate, baked at 150° C. (300° F.) was unsatisfactory, as the cement was slowly attacked by the solutions. Joints made similarly with a mixture of sodium silicate (grade S) and silica-gel lasted somewhat longer, but were not permanent.

The box finally adopted (fig. 4) for this purpose consisted of a heavy steel box, screwed together so as to be water-tight without cement. This box was lined with plate-glass strips, with edges accurately ground. The glass box was not absolutely water-tight, but tests showed that there was no significant electrical leakage through the joints. A platinum-gauze anode and two sheet cathodes, usually of steel, were held in place at the top by a bakelite frame, and at the bottom by strips of thin glass (not shown in the figure) that covered the bottom of the box. The cross section of the solution was 5 by 5 cm (2 by 2 inches) and the two cathodes were, respectively, 5 and 10 cm (2 and 4 inches) from the anode. The primary ratio was therefore 2:1. This ratio was adopted in order to cover a wider range of plating conditions than will yield bright deposits with a greater ratio, such as 5 to 1.

The box was set in a water thermostat. The temperature of the latter was controlled so as to maintain the desired temperature in the cell, which as the result of the passage of current was usually a few degrees higher than that of the surrounding water bath. The solution in the box was maintained at the designated temperatures to ±1° C. Unless otherwise stated the time of deposition in each experiment was 30 minutes.

In order to determine in the same experiment the throwing power and the cathode efficiencies on the two plates, it was necessary to measure the currents passing to the two cathodes. In the initial experiments this was done by means of two copper coulometers, each connected in series with a cathode. An adjustable resistance was also in one circuit in order to maintain the two cathodes at the same potential with respect to the anode. This arrangement yielded reliable results, but was cumbersome and required very careful adjustment. The results showed that the secondary current ratio was almost exactly 2:1, and never less than 1.9:1. This shows that there was no appreciable difference between the polarizations at the current densities used on the two cathodes.

In the later experiments precision ammeters were substituted for the copper coulometers. The currents were sufficiently constant to permit the number of coulombs to be measured within about 2 per cent, which precision was adequate, as the cathode efficiencies were seldom reproducible within 5 per cent of their values. Thus in duplicate experiments the cathode efficiencies on the two plates might be in one case 10.3 and 17.6 per cent, and in another 9.9 and 18.2 per cent.

As the current distribution was practically 2:1, the measurements of throwing power really represented cathode efficiency determina-

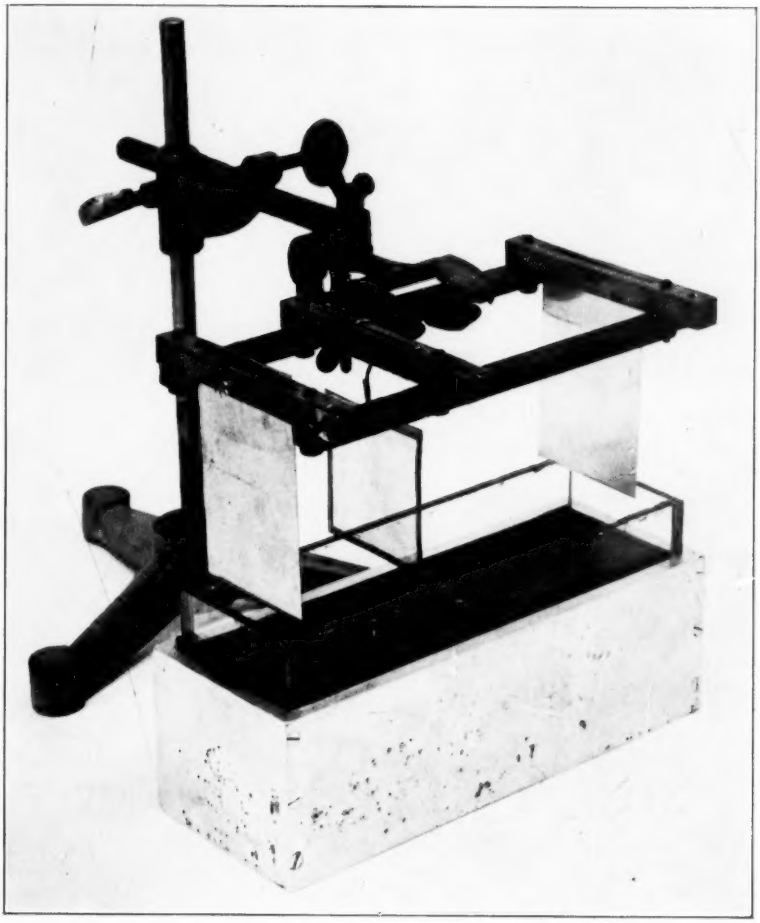

FIGURE 4.—*Throwing power box*

A steel box lined with glass. Platinum gauze anode and steel cathodes

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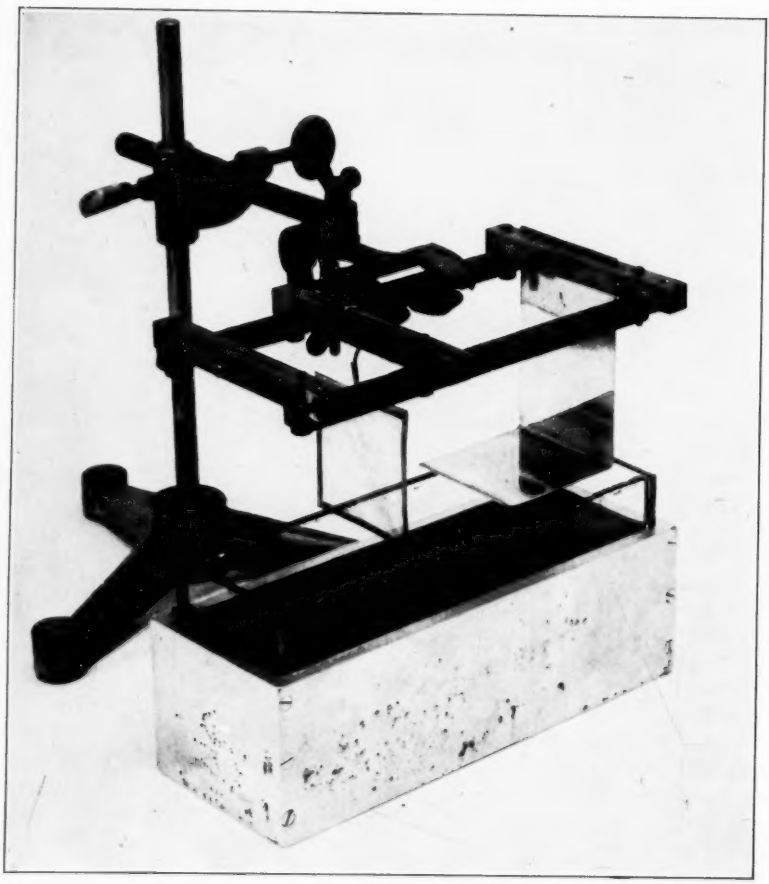

FIGURE 5.—*Arrangement for bent cathode test*

Platinum gauze anode and copper cathode.

tions, which might have been made in other apparatus than the throwing-power box, which, for this purpose, was simply a means of obtaining definite and uniform current densities on plane parallel plates of known dimensions. The results in the box were, however, more significant than if, as is all to common practice, the cathodes were suspended in jars of larger cross section, in which case the current densities would not have been so nearly uniform over the cathodes, and the recorded cathode efficiencies would have been simply averages for the existing current densities.

3. PLATING RANGE

All deposits produced in the throwing-power experiments were classified (by two observers) as milky (M), bright (Br), frosty (F), and burnt (Bu). As there are no sharp lines between these groups, the designations were necessarily approximate. Additional experiments were made near the dividing lines, in order to fix the latter as definitely as possible. One reason that the data of this study may not agree exactly with those of other observers, is that in our experiments the current densities were more uniform than in most of the other recorded measurements. Another reason is that these deposits were made upon steel, on which the plating range is narrower than on copper or brass.

4. BENT CATHODE TESTS

In order to determine whether the results for throwing power represent, or are at least parallel to, those that would be obtained in actual plating, experiments were made with bent cathodes, such as have been used by Sizelove and by Pinner and Baker. In this investigation the test was made somewhat more quantitative and more closely related to the throwing power by the following modifications.

As shown in Figure 5, the cathode, usually of polished copper, was 5 cm (2 inches) wide, and was bent at a sharp right angle, so that the horizontal portion, and also the vertical portion that was immersed in the solution, were each 5 by 5 cm (2 by 2 inches). The cathode was placed at one end of the throwing-power box with the horizontal portion resting on the bottom; and a plane anode, which may be of sheet lead (though the platinum gauze was used in most of our tests) was placed at a distance of 10 cm (4 inches) from the vertical portion of the cathode. The minimum distances from the anode to the horizontal and vertical parts of the cathode were therefore 5 and 10 cm (2 and 4 inches), respectively. Hence, this ratio was 2 to 1, just as in the throwing-power experiments. Actually the current densities were not uniform on the two parts of the cathode, but decreased as the angle was approached. The extent to which the cathode was covered defined the covering power, which, as will be seen, was practically parallel to the throwing power as previously measured. Preliminary tests showed that the area covered did not change noticeably after plating for five minutes. This period was, therefore, employed in the experiments.

VI. RESULTS OBTAINED

In the following tables the data have been assembled in such a way as to emphasize the effects of each variable. Even then it is necessary to refer to different tables to bring out the full comparisons,

as it would involve too much repetition to include all comparable data in each table. The experiment numbers refer to the order in which they were conducted, and are included simply for reference. The solution numbers refer to Table 1, which contains details regarding composition and preparation.

The average current density is the arithmetical mean of the current densities on the near and far plates. As previously noted, the observed current densities were always in the ratio of 2 to 1, within a few per cent. The actual current density on the near plate was, therefore,

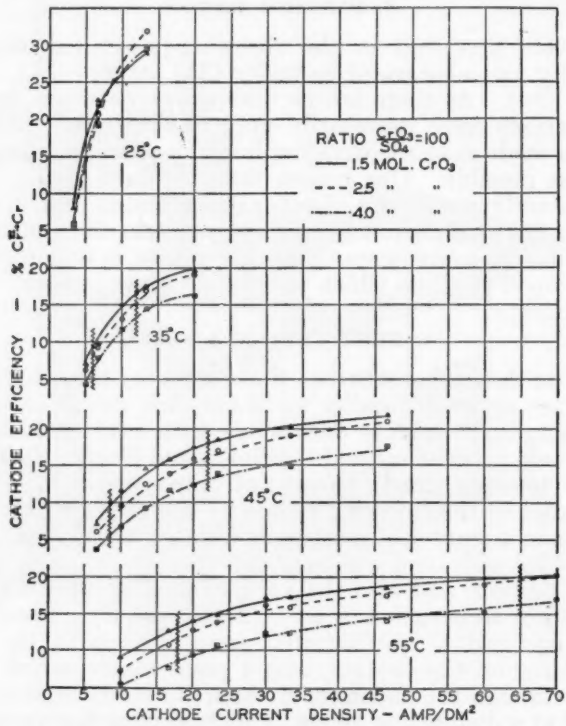

FIGURE 6.—*Effect of temperature and chromic acid concentration on cathode efficiency*

Bright deposits obtained between wavy lines.

practically 1.33 times the average and on the far plate 0.67 times the average.

The voltage represents the total drop between the anode and cathode. The numerical values of voltage apply only to the arrangement and dimensions of this box, but they indicate qualitatively the relative voltages that would be required for any given arrangement in commercial baths.

The cathode efficiencies have been computed from the readings of current and time and the weights of deposit. They are all based on hexavalent chromium. Tests showed that with polished cathodes they were reproducible to within about 5 per cent of their values. As the cathode efficiencies represent the most important factor in chromium plating, they have been plotted in Figures 6 to 9.

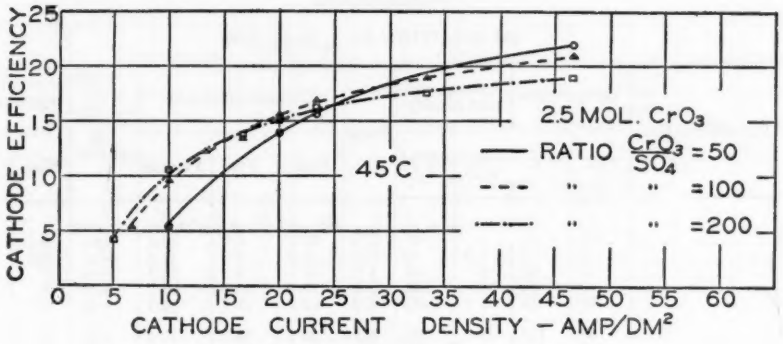

FIGURE 7.—*Effect of sulphate ratio on cathode efficiency*

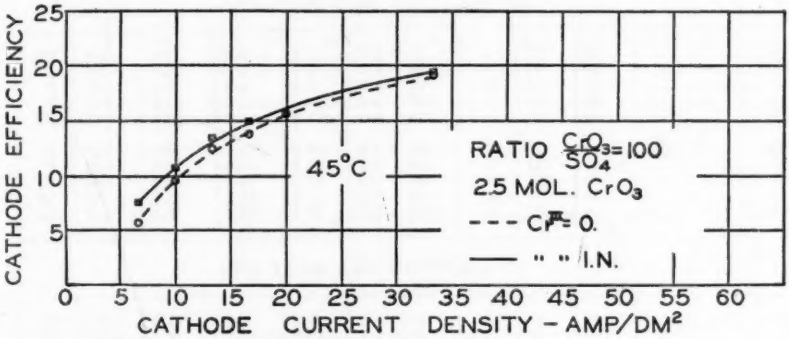

FIGURE 8.—*Effect of trivalent chromium on cathode efficiency*

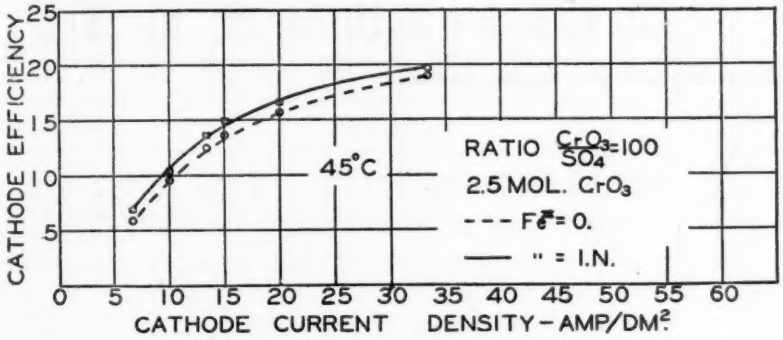

FIGURE 9.—*Effect of iron on cathode efficiency*

TABLE 2.—*Effect of temperature and current density on throwing power*

$CrO_3/SO_4=100$

(A) SOLUTION No. 1, 150 g/L CrO_3

Experiment No.	Temperature		Average current density		Volts	Cathode efficiency			Throwing power	Appearance[1]	
	°C.	°F.	Amp./dm.²	Amp./ft.²		Near	Far	Average		Near	Far
						Per cent	*Per cent*	*Per cent*	*Per cent*		
1	25	77	5	47	3.9	22.6	8.0	15.3	−204	Bu	M
7	35	95	7.5	70	4.1	16.3	6.9	11.6	−127	Br	Br
10	35	95	10	93	4.6	17.4	9.5	13.5	−84	F	Br
13	35	95	15	140	5.4	19.6	13.8	16.7	−43	F	Br
16	45	113	15	140	5.2	17.7	11.7	14.7	−50	Br	Br
19	45	113	25	230	6.7	20.2	15.7	17.9	−26	F	Br
22	45	113	35	325	7.8	21.7	18.2	19.9	−19	F	F
25	55	131	25	230	6.2	16.9	12.7	14.8	−33	Br	M
28	55	131	35	325	7.6	18.5	14.7	16.6	−23	Br	Br
31	55	131	45	420	8.9	19.6	17.2	18.4	−13	Br	Br

(B) SOLUTION No. 2, 250 g/L CrO_3

2	25	77	5	47	3.9	19.2	5.4	12.3	−295	Bu	M
8	35	95	7.5	70	3.9	14.3	6.5	10.4	−108	F	M
11	35	95	10	93	4.3	17.2	9.3	13.2	−87	F	Br
14	35	95	15	140	4.8	19.3	12.0	15.6	−58	F	Br
17	45	113	15	140	4.6	15.9	9.9	12.9	−65	Br	Br
20	45	113	25	230	5.8	19.0	13.6	16.3	−27	F	Br
23	45	113	35	325	6.8	21.0	17.0	19.0	−23	F	F
26	55	131	25	230	5.5	15.7	10.8	13.3	−46	Br	M
29	55	131	35	325	6.4	17.9	13.8	15.8	−28	Br	Br
32	55	131	45	420	7.5	19.5	16.7	18.1	−14	Br	Br

(C) SOLUTION No. 3, 400 g/L CrO_3

3	25	77	5	47	3.9	21.8	5.9	13.8	−312	Bu	M
9	35	95	7.5	70	3.8	12.2	4.1	8.1	−177	Br	M
12	35	95	10	93	4.1	19.5	7.7	11.1	−87	F	Br
15	35	95	15	140	4.7	15.9	11.3	13.6	−59	F	Br
18	45	113	15	140	4.5	12.2	6.7	9.5	−85	Br	Br
21	45	113	25	230	5.4	14.4	12.0	13.2	−28	F	Br
24	45	113	35	325	6.2	17.9	14.2	16.0	−25	F	F
27	55	131	25	230	5.1	11.6	7.7	9.6	−52	Br	M
30	55	131	35	325	6.0	14.1	10.8	12.5	−29	Br	Br
33	55	131	45	420	6.8	15.2	12.6	13.9	−18	Br	Br

[1] M=milky; Br=bright,; F=frosty; Bu=burnt.

TABLE 3.—*Effect of sulphate ratio on throwing power*

(A) $CrO_3/SO_4=50$

Experiment No.	Solution No.	Temperature		Average current density		Volts	Cathode efficiency			Throwing power	Appearance	
		°C.	°F.	Amp./dm.²	Amp./ft.²		Near	Far	Average		Near	Far
							Per cent	*Per cent*	*Per cent*	*Per cent*		
48	7	45	113	15	140	5.0	16.5	9.5	13.0	−61	Br	Br
43	8	35	95	15	140	4.8	Current variable			−117	F	Br
37	8	45	113	7.5	70	3.3				-------	M	No dep.
35	8	45	113	15	140	4.7	13.9	5.4	9.7	−154	Br	M
40	8	45	113	35	325	6.7	21.7	15.9	18.8	−34	F	Br
46	8	55	131	15	140	4.4	Current variable			−350	Br	M
50	9	45	113	15	140	4.4	11.8	6.0	8.9	−113	Br	M
							(B) $CrO_3/SO_4=200$					
47	4	45	113	15	140	5.0	17.3	12.4	14.8	−38	Br	Br
54	5	35	95	7.5	70	3.9	14.5	9.0	11.7	−62	Br	Br
41	5	35	95	10	93	4.1	16.4	12.1	14.2	−37	F	Br
42	5	35	95	15	140	4.8	18.6	13.3	15.9	−37	F	Br
36	5	45	113	7.5	70	3.8	10.7	4.2	7.5	−143	Br	M
34	5	45	113	15	140	4.7	15.2	10.4	12.8	−52	Br	Br
38	5	45	113	25	230	5.7	17.3	13.7	15.5	−27	F	Br
39	5	45	113	35	325	6.8	18.9	16.4	17.7	−15	F	F
45	5	55	131	15	140	4.4	11.3	5.4	8.4	−102	M	M
44	5	55	131	35	325	6.4	15.0	13.4	14.2	−13	Br	Br
53	6	35	95	7.5	70	3.9	14.5	9.0	11.7	−62	Br	Br
49	6	45	113	15	140	4.4	12.2	7.3	9.8	−62	Br	M

TABLE 4.—*Effects of soluble additions on throwing power*

250 g/L CrO_3

(A) $Na_2Cr_2O_7$

Experiment No.	Solution No.	Temperature		Average current density		Volts	Cathode efficiency			Throwing power	Appearance	
		°C.	°F.	Amp./dm.²	Amp./ft.²		Near	Far	Average		Near	Far
							Per cent	*Per cent*	*Per cent*	*Per cent*		
56	10	35	95	7.5	70	4.0	12.6	6.0	9.3	−103	F	M
55	10	45	113	15	140	4.9	11.8	7.7	9.7	−50	Br	Br
57	11	45	113	15	140	4.8	6.2	3.1	4.6	−100	Br	Br
							(B) H_3BO_3					
58	12	45	113	15	140	4.4	15.8	9.4	12.6	−64	Br	Br
59	13	45	113	15	140	4.5	15.6	9.2	12.4	−67	Br	Br

TABLE 5.—*Effect of trivalent chromium*

Experiment No.	Solution No.	Cr^{III} N	Temperature		Average current density		Volts	Cathode efficiency			Throwing power	Appearance	
			°C.	°F.	Amp./dm.²	Amp./ft.²		Near	Far	Average		Near	Far
								Per cent	*Per cent*	*Per cent*	*Per cent*		
61	14	0.05	45	113	15	140	4.5	15.6	9.1	12.4	−70	Br	Br
62	15	.16	45	113	15	140	4.6	16.4	9.8	13.1	−64	Br	Br
63	15	.16	55	131	35	325	6.7	18.6	14.2	16.4	−30	Br	Br
64	16	.18	45	113	15	140	4.6	16.4	9.8	13.1	−64	Br	Br
65	16	.18	55	131	35	325	7.3	18.8	14.2	16.5	−27	Br	Br
66	18	.50	45	113	15	140	4.8	16.3	10.5	13.4	−57	Br	Br
67	18	.50	55	131	35	325	7.3	18.1	14.0	16.0	−27	Br	Br
80	20	1.00	45	113	10	93	4.6	13.6	7.9	10.8	−71	Br	M
68	20	1.00	45	113	15	140	5.5	15.6	10.7	13.1	−43	Br	Br
81	20	1.00	45	113	25	230	7.1	19.2	15.1	17.1	−26	F	Br
69	20	1.00	55	131	35	325	8.8	17.0	14.0	15.5	−22	Br	Br
74	21	2.0	45	113	15	140	7.0	15.1	11.6	13.4	−29	Br	Br
75	21	2.0	55	131	35	325	12+	Insufficient voltage.					
76	22	2.5	45	113	15	140	10	Deposits rough and discolored.					
77	22	2.5	55	131	35	325	12+	Insufficient voltage.					
70	17	.50	45	113	15	140	6.0	17.7	12.3	15.0	−43	Br	Br
71	19	.50	45	113	15	140	4.5	12.2	7.4	9.8	−64	Br	Br
72	24	.50	45	113	15	140	4.9	14.9	10.1	12.5	−46	Br	Br
73	25	.50	45	113	15	140	4.9	15.1	8.0	11.6	−86	Br	Br
78	23	.80	45	113	15	140	4.7	13.2	8.1	10.7	−61	Br	Br
79	23	.80	55	131	35	325	6.8	14.3	11.3	12.8	−24	Br	Br

TABLE 6.—*Effect of iron*

Experiment No.	Solution No.	Fe^{III} N	Temperature		Average current density		Volts	Cathode efficiency			Throwing power	Appearance	
			°C.	°F.	Amp./dm.²	Amp./ft.²		Near	Far	Average		Near	Far
								Per cent	*Per cent*	*Per cent*	*Per cent*		
83	26	0.20	45	113	15	140	4.6	15.9	9.2	12.6	−71	Br	Br
84	26	.20	55	131	35	325	6.9	17.7	13.8	15.7	−27	Br	Br
85	27	.50	45	113	15	140	4.7	16.0	10.2	13.1	−56	Br	Br
86	27	.50	55	131	35	325	7.2	17.8	13.8	15.8	−27	F	Br
89	28	1.0	45	113	10	93	4.4	13.7	6.9	10.3	−105	Br	M
87	28	1.0	45	113	15	140	5.1	16.3	10.4	13.4	−55	Br	Br
90	28	1.0	45	113	25	230	6.8	19.7	15.0	17.3	−29	F	Br
88	28	1.0	55	131	35	325	8.3	18.2	14.5	16.3	−25	F	Br
96	29	2.0	45	113	15	140	7.8	16.7	12.0	14.4	−37	F	Br
97	29	2.0	55	113	35	325	12+	Insufficient voltage.					
92	30	1.0	45	113	15	140	7.5	17.6	12.5	15.0	−41	Br	Br
93	31	1.0	45	113	15	140	4.6	13.8	8.8	11.3	−56	F	Br
94	32	1.0	45	113	15	140	5.3	15.5	11.5	13.5	−47	F	M
95	33	1.0	45	113	15	140	5.3	15.5	7.0	11.3	−119	Br	Br
								$Fe^{III}+Cr^{III}$					
91	34	0.5 .5	45	113	15	140	5.5	16.4	10.6	13.5	−58	Br	Br
100	35	.05 .06	45	113	15	140	4.6	16.2	9.2	12.7	−71	Br	Br

TABLE 7.—*Effect of composition of base metal on throwing power*

250 g/L CrO_3; CrO_3/SO_4=100; 45° C. (113° F.); 15 amp./dm.²

Experiment No.	Base metal	Volts	Cathode efficiency			Throwing power	Appearance	
			Near	Far	Average		Near	Far
			Per cent	*Per cent*	*Per cent*	*Per cent*		
17	Steel	4.6	15.9	9.9	12.9	−65	Br	Br
101	Copper	4.5	16.0	8.2	12.1	−85	Br	Br
102	Brass	4.5	16.4	9.5	12.9	−70	Br	Br
103	Nickel [1]	4.5	16.3	8.5	12.4	−81	Br	Br

[1] Nickel-plated brass.

VII. DISCUSSION OF RESULTS

As the throwing power may be affected by each of a number of variables, it is difficult, if not impossible, to select any one set of conditions as best. Instead, it will be most convenient to consider independently the effect of each variable. The actual choice of operating conditions will usually represent a compromise, owing to the limitations that may be imposed in a given plant by the character of work to be plated, the available voltage, and other factors.

1. TEMPERATURE AND CURRENT DENSITY

Table 2 shows clearly that raising the current density at a fixed temperature increases the throwing power; while an elevation in temperature at a fixed current density decreases the throwing power. The best throwing power in the range of bright deposits is obtained, however, at relatively high temperatures and current densities. The reason for this is evident from Figure 6, in which it is shown that as the temperature is increased, the cathode efficiencies become more uniform within the range of bright deposits.

As the temperature of the bath is raised its conductivity is increased, and hence the voltage required to produce a given current density is decreased. But to produce bright deposits at the higher temperature the current density must be raised more than in proportion to the increase in conductivity. Consequently, a higher voltage is needed at a high temperature, such as 55° C. (131° F.), to produce bright deposits along with the superior throwing power than at some lower temperature.

Practically, it is advisable to employ as high a temperature and corresponding current density as other conditions permit. At room temperature, 25° C. (77° F.), it is possible to produce bright deposits upon copper or brass (but not on steel) when the current ratio is 2:1. Hence, if articles are satisfactorily plated at so low a temperature, they are probably of such a shape and in such a position in the bath that the current density is nearly uniform over each article. At temperatures up to 55° C. (131° F.) with appropriately high current densities, the throwing power approaches zero, which is the highest value that can be expected in view of the negligible effect of polarization. If, however, a 6-volt generator is used, a potential of not more than 5 volts is generally available between the electrodes. In that case a lower temperature, such as from 35° to 45° C. (95° to 113° F.)

and as high current densities as will produce bright deposits, should be used. The actual temperature selected must be maintained within about ±2° C. (±4° F.) to obtain uniform results.

2. COMPOSITION OF SOLUTIONS

(a) CHROMIC ACID

Table 2 shows that as the concentration of chromic acid is raised while the ratio of chromic acid to sulphate is kept constant, the throwing power for given conditions decreases. This is because in every case, as shown in Figure 6, the cathode efficiencies are higher and more uniform in the more dilute solutions. When the maximum throwing power for a given current density is desired, a relatively dilute solution is advantageous. As, however, the less concentrated solution has a lower conductivity, a higher voltage is needed to produce a given current density. Thus in the box, at 45° C. and 15 amp./dm^2, for 150, 250, and 400 g/L CrO_3, the voltages are, respectively, 5.2, 4.6, and 4.5, and the throwing powers are −50, −65, and −85 per cent. Suppose, however, that instead of having a constant average current density, a fixed potential; for example, 5 volts, is applied. Then by graphic interpolation it may be seen that in the three solutions the throwing powers will be, respectively, about −55, −45, and −40 per cent. Therefore, for a given voltage the more concentrated solution has a better throwing power. The best concentration will depend on the conditions and class of work. Owing to the larger loss by "drag out" of concentrated solutions, and to the higher voltage required for dilute solutions, an intermediate concentration of about 250 g/L (33 oz./gal.) of chromic acid is generally suitable.

(b) SULPHATE

The actual content of sulphate is not so important as the ratio of chromic acid to sulphate. In this paper this ratio is expressed by weight; thus the statement "$\frac{CrO_3}{SO_4}=100$" means that the actual concentrations of chromic acid and sulphate (expressed in either g/L or oz./gal.) are in the ratio of 100:1. In many other papers on chromium plating this ratio has been expressed in terms of the molarity of chromic acid and the normality of sulphuric acid, thus for the above ratio, $\frac{M\ CrO_3}{N\ SO_4}=50$. The latter ratio for any given solution is practically one-half that computed by weight.

Previous experiments have shown that the form in which the sulphate is added is immaterial. The concentrations of sulphate, SO_4, given in this paper are for practical purposes the same as those of sulphuric acid, H_2SO_4, to be added. If other sulphates such as sodium or chromium sulphate are employed, chemically equivalent weights should be used.

As shown by comparison of Tables 2 and 3, a solution with the ratio of $\frac{CrO_3}{SO_4}=100$, which was found by Haring and Barrows to give the best average cathode efficiency, does not have as good throwing power as one with a smaller sulphate content; for example,

$\frac{CrO_3}{SO_4}=200$. As shown in Figure 7, the improvement with the lower sulphate content is due to the fact that the cathode efficiency is thereby made greater at low current densities and less at high current densities. An increase in the sulphate content to make the ratio 50:1 greatly decreases throwing power. A smaller sulphate content than 200:1 is objectionable because brown streaks then form on the deposits. For practical purposes, the sulphate content should, therefore, be between 100:1 and 200:1, which latter ratio leads to slightly better throwing power. It was not found possible in these tests to detect effects due to small variations in the sulphate ratio, such as have been reported by Pinner and Baker from experiments with bent cathodes.

(c) SOLUBLE ADDITIONS

No attempt was made to study the effects of all the substances that have been suggested as additions to chromium-plating baths. The two selected were sodium dichromate and boric acid, for each of which definite claims have been made.

(1) *Sodium dichromate.*—The results in Table 4 show that the addition of a large amount of sodium dichromate (solution 10) increases the throwing power from −65 per cent (experiment 17, Table 2) to −50 per cent (experiment 55, Table 4). That this slight increase in throwing power is due principally to an effective reduction in the sulphate ratio by the addition of the dichromate is shown by the fact that under these conditions a solution (No. 5) containing the same amount of free chromic acid, but less sulphate, has a throwing power of −52 per cent (experiment 34, Table 3). If, however, the dichromate is added to a solution of low sulphate content (to produce solution No. 11), the throwing power is −100 per cent (experiment 57, Table 4), which is much worse than that obtained without the dichromate. It seems, therefore, that any apparent advantage of the sodium dichromate can be more easily obtained by simply reducing the sulphate content of the solution. Moreover the dichromate decreases the conductivity and for given conditions requires a slightly higher voltage (4.9 volts in experiment 55, Table 4) than the plain solution (4.7 volts in experiment 34, Table 3); while solution 6, which contains CrO_3 equivalent to both the CrO_3 and $Na_2Cr_2O_7$ present in solution 10, requires only 4.4 volts and gives a throwing power of −62 per cent (experiment 49, Table 3).

(2) *Boric acid.*—Concentrations of boric acid up to 0.25 M (15 g/L or 2 oz./gal.) have no appreciable effect upon the throwing power.

(d) TRIVALENT CHROMIUM

The possible effects of trivalent chromium upon the throwing power are important, because this substance is always present in commercial plating baths and has sometimes been added intentionally.

The results in Table 5 and Figure 8 show that small concentrations of trivalent chromium have no measurable effect. When the Cr^{III} is 0.05 *N*; that is, exactly equivalent to the sulphate content, a condition that exists if chromium sulphate is used in preparing a new solution; the throwing power is practically the same as in the standard solution under the same conditions. Not until the concentration is greater than 0.5 *N* can any marked effect on throwing power

be detected. High concentrations, such as 1.0 and 2.0 *N* (experiments 68 and 74, Table 5) lead to a definite improvement in throwing power, to −43 and −29 per cent, as compared with −65 per cent with the standard solution. This effect is undoubtedly due to the removal by the trivalent chromium of part of the free chromic acid to form chromium chromate. It may be significant that the throwing power with 2.5 *M* CrO_3 and 1.0 *N* Cr^{III} is about the same (−43 per cent) as with 1.5 *M* CrO_3 alone (−50 per cent), (experiment 16, Table 2). This ratio corresponds to the formation of $Cr(HCrO_4)_3$. As the former solution required 5.5 volts, and the latter 5.2 volts, it is evident that any improvement in throwing power brought about by the presence of a large amount of trivalent chromium, can be more easily obtained by using a more dilute solution without trivalent chromium. Moreover, as shown by Schneidewind[9] trivalent chromium reduces the range within which bright deposits can be obtained, which observation was confirmed in these experiments. It is evident, therefore, that no real advantage is gained by adding trivalent chromium or by allowing it to reach a high concentration.

(e) IRON

Most chromium plating solutions are kept in steel tanks, which are slowly attacked, thus introducing small amounts of iron into the baths. If steel anodes are used, considerable iron may pass into solution. It has been generally recognized that a large content of this element is objectionable as it decreases the conductivity and the plating range. It has been claimed that small concentrations of iron are beneficial, and it is sometimes intentionally added; for example, in the form of iron chromate, or of iron chromite (the mineral chromite).

The data in Table 6 and Figure 9 show that iron behaves very similarly to trivalent chromium in these solutions. Small concentrations, either alone (experiments 83 and 84) or in the presence of trivalent chromium (experiment 100) have no beneficial effect on the throwing power. Larger amounts increase the throwing power, but not quite so much as do equivalent concentrations of trivalent chromium. It appears probable that the iron is present as a ferric chromate, the formation of which removes an equivalent amount of the free chromic acid. This is confirmed by the higher resistivity, which requires an increased voltage to produce a given current density. This increased voltage, and the fact that the bright plating range is decreased by the presence of the iron, show that the presence of large amounts of iron is undesirable. It was found in our tests that the rate of solution of the mineral chromite, even when finely divided, in warm chromic acid solutions, is very slow, and that even after several days contact with an excess of the mineral, only small amounts of trivalent chromium and iron are thus introduced into the solution.

3. COMPOSITION AND CONDITION OF BASE METAL

All of the experiments recorded in Tables 2 to 6 were made on polished steel cathodes. Steel was selected because it was not appreciably attacked by the chromic acid in the 30-minute periods used

[9] See footnote 3, p. 28.

in most of the experiments. Hence, there was no iron dissolved from the back of the plates during the experiments, and accurate weighings were facilitated.

Early experiments with cold-rolled steel, which had a fairly bright surface, showed that it was difficult to obtain reproducible results for cathode efficiency or throwing power. When the cathodes were buffed to a uniformly bright surface the results were much more concordant. That the cathode efficiencies, especially at low current densities, are greatly affected by the condition of the surface is shown by an experiment not recorded in the tables. In this test sand-blasted steel cathodes were used, and under standard conditions the cathode efficiencies were about 10 and 1 per cent, respectively, on the near and far plates, representing a throwing power of less than −1,000 per cent.

Undoubtedly these differences in cathode efficiency are associated with differences in hydrogen overvoltage on the surfaces. It is generally recognized that the hydrogen overvoltage is decreased by roughening the surface. This facilitates hydrogen evolution and thus reduces the cathode efficiency of chromium deposition. It is therefore advantageous to deposit chromium on highly polished metal.

A few experiments were made on the influence of a brief preliminary reversal of current upon the throwing power with steel cathodes. No effect could be detected. It is at least probable that the beneficial effect sometimes obtained by reversing the current on steel just before plating with chromium is due to the cleaning action caused by the anodic treatment with chromic acid.

The data in Table 7 show that the cathode efficiency and throwing power are also affected by the composition of the base metal. The throwing power on steel and brass is slightly better than on copper and nickel. The differences are due almost entirely to the cathode efficiencies at the low current densities. While these differences in throwing power are not great, they are sufficiently definite to affect also the covering power to be discussed in the next section.

4. BENT CATHODE TESTS

It was found that under the conditions used by us, the extent of the covering by chromium on the bent cathodes was fairly reproducible. Except as otherwise noted, copper was used in the bent cathode tests, in order to intensify the contrast between the appearance of the base metal and the chromium. It was found impracticable to photograph satisfactorily these bent cathodes, owing to the reflections from the polished copper and chromium. Therefore, line drawings have been used in Figures 10 to 16 to illustrate the results.

Figure 10 shows that there is approximate parallelism between the throwing power as previously measured and the extent of covering. This relation was confirmed by applying to the bent cathodes two sets of conditions, each of which had yielded about the same throwing power. It was then found that the covering power was also practically the same under the two conditions.

The numerical values for throwing power, included with Figures 10 to 16, are based on measurements with steel, on which as above noted and also illustrated in Figure 16, the throwing power was

slightly better than on copper. Hence, these values do not exactly correspond with those for copper, of which the bent cathodes con-

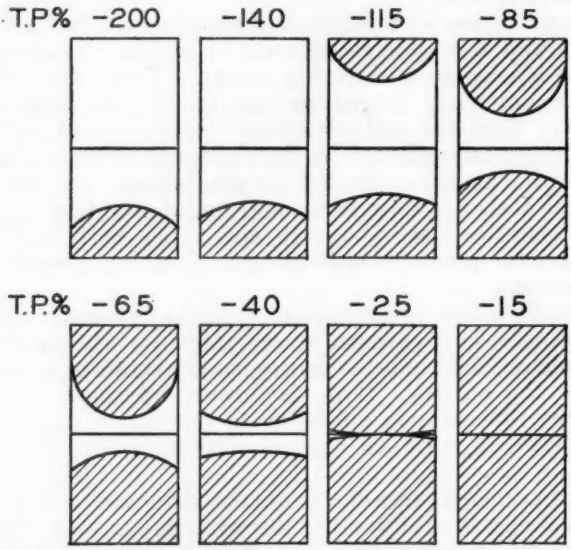

FIGURE 10.—*Relation of throwing power (on steel) and covering power (on copper)*

These and the following diagrams represent the appearance of cathodes bent at right angles when plated, and subsequently flattened out. The shaded portions are those covered with chromium.

sisted. As, however, all results for throwing power are only relative, the effects of different variables upon both the throwing power and covering power are illustrated by these diagrams.

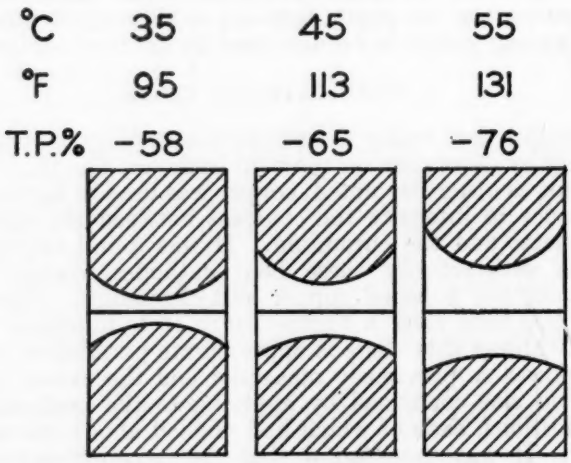

FIGURE 11.—*Effect of temperature on covering power*

Figures 11 and 12 show clearly that an increase in temperature lessens the covering power, while an increase in current density improves it. The effects of chromic acid, shown in Figure 13, are not

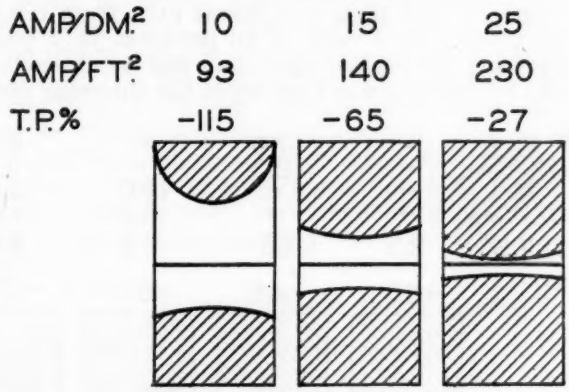

FIGURE 12.—*Effect of current density on covering power*

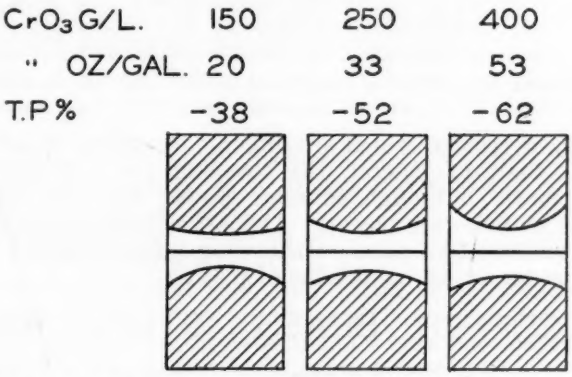

FIGURE 13.—*Effect of chromic acid concentration on covering power*

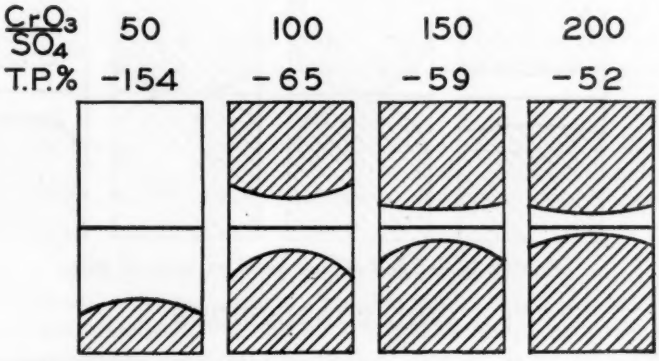

FIGURE 14.—*Effect of sulphate concentration on covering power*

great but correspond approximately to the throwing powers. Similarly, in Figure 14, variations in sulphate ratio from 100 to 200 have only a small effect, but a ratio of 50 produces very poor covering. Figure 15 shows that trivalent chromium and iron have less beneficial effects on the covering power than upon the throwing power.

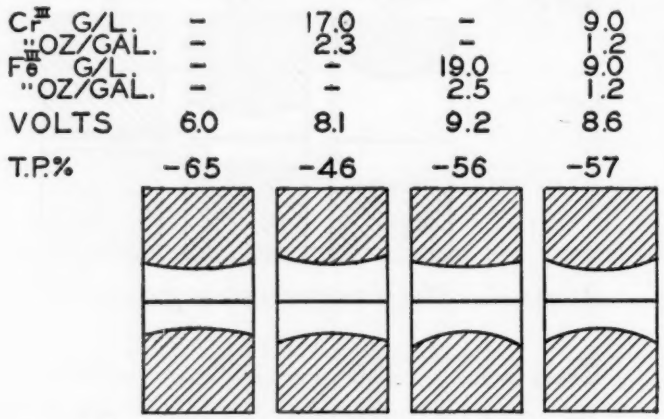

FIGURE 15.—*Effect of trivalent chromium and iron on covering power*

From these results, which are difficult to express quantitatively, it is evident that, in general, the covering power is parallel to the throwing power, although covering power does not portray small differences in throwing power. At least it may be safely concluded that the quantitative data on throwing power indicate the relative behavior under actual conditions of plating.

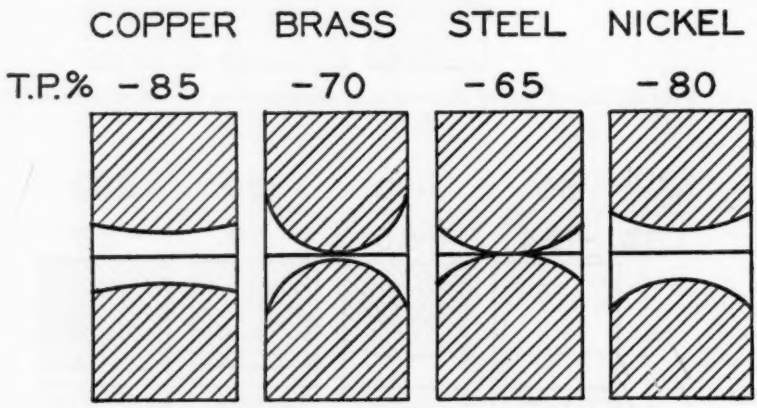

FIGURE 16.—*Effect of base metal on covering power*

VIII. CONCLUSIONS

1. Throwing power in chromium plating is determined almost entirely by the relative cathode efficiencies at the maximum and minimum current densities. An improvement in throwing power can be effected by any means which makes these efficiencies more nearly equal.

2. An increase in temperature lowers the throwing power.

3. An increase in current density raises the throwing power.

4. By increasing both the temperature and the current density the throwing power is made greater than at lower temperatures and current densities. As the range of bright deposits is wider at high temperatures, these conditions are the most favorable. However, if the available voltage is limited to about 6 volts, an intermediate temperature and current density will yield best results.

5. For a given current density, better throwing power is obtained in dilute than in concentrated chromic acid solutions. If the available voltage is low, better throwing power is obtained in the more concentrated baths.

6. A ratio of $\frac{CrO_3}{SO_4}=200$ yields better throwing power than a ratio of 100 and very much better than a ratio of 50.

7. Large additions of sodium dichromate to a solution with a sulphate ratio of 100 slightly increase the throwing power, probably by changing the effective sulphate ratio. If the latter is initially 200, sodium dichromate is detrimental.

8. Boric acid has no measurable effect on the throwing power.

9. Small concentrations of trivalent chromium have no effect. Large concentrations slightly improve the throwing power, making it equal to that in a more dilute solution. As the trivalent chromium reduces the conductivity and the plating range, it is not a desirable constituent.

10. Iron has almost exactly the same effects on throwing power as trivalent chromium, but has a greater detrimental effect on the conductivity and plating range.

11. The throwing power is much better on highly polished than on dull metal. On sand-blasted metal it is very poor.

12. The throwing power is slightly better on steel and brass than on copper and nickel.

13. The covering power as determined with a bent cathode is practically parallel to the measured throwing power.

14. The best throwing power (−13 per cent) with bright deposits was obtained in a solution containing 250 g/L (33 oz./gal.) of CrO_3, 1.25 g/L (0.17 oz./gal.) of SO_4, at a temperature of 55° C. (131° F.) and an average current density of 35 amp./dm^2 (325 amp./ft.^{2}). This required in the box, 6.4 volts. Such conditions are suggested for use when a voltage above 6 is available, and when the best attainable throwing power is desired.

15. When the voltage is limited to only 5 volts at the tank, a fair throwing power (about −60 per cent) can be obtained with 400 g/L (55 oz./gal.) of CrO_3 and 2 g/L (0.27 oz./gal.) of SO_4, at a temperature of 45° C. (113° F.) and an average current density of 15 amp./dm.^{2} (140 amp./ft.^{2}).

16. In the latter solution, at a temperature of 35° C. (95° F.) and an average current density of 7.5 amp./dm^2 (70 amp./ft.^{2}) a throwing power of about −60 per cent is also obtained. This is usually satisfactory if the articles are not of very irregular shape or are favorably placed in the tank.

WASHINGTON, September 27, 1929.

INFLUENCE OF MAGNESIA, FERRIC OXIDE, AND SODA UPON THE TEMPERATURE OF LIQUID FORMATION IN CERTAIN PORTLAND CEMENT MIXTURES

By W. C. Hansen

ABSTRACT

A study has been made of the influence of ferric oxide, magnesia, and soda upon the temperature at which melting starts when they are added individually and collectively to mixtures of lime, alumina, and silica. The mixtures had compositions similar to those of Portland cement. It was found that these mixtures with lime, alumina, and silica started to melt at 1,455° C. When ferric oxide was added, the temperature of liquid formation was reduced to 1,340° C.; with magnesia, to 1,375° C.; with soda, to 1,430° C.; with ferric oxide and magnesia, to 1,300° C.; and with the three added components, to 1,280° C. The compounds observed at equilibrium in the clinkers made from lime, alumina, silica, ferric oxide, and magnesia were found by microscopic and X-ray methods to be $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, and MgO.

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I. INTRODUCTION

The studies to be reported here were undertaken as a continuation of a program to determine the manner in which each component occurs in Portland cement and the rôle played by each during the manufacture and utilization of the cement.

The work of previous investigators in this country[1] has shown that $3CaO.SiO_2$ is the principal hydraulic compound of Portland cement. This compound is formed by the reaction[2] $3CaO+SiO_2+\text{heat} \rightarrow 2CaO.SiO_2+CaO+\text{heat} \rightarrow 3CaO.SiO_2$. The formation of $2CaO.SiO_2$ is rapid at temperatures around 1,400° to 1,500° C., but the reaction of $2CaO.SiO_2+CaO$ to form $3CaO.SiO_2$ is extremely slow at these temperatures. Certain other components added to the system $CaO+SiO_2$ cause the formation of liquid at temperatures below 1,500° C., thus speeding up the reaction producing $3CaO.SiO_2$.

[1] G. A. Rankin, J. Ind. Eng. Chem., **7**, p. 466; 1915, P. H. Bates and A. A. Klein, B. S. Tech. Paper No. 73; 1917.

[2] G. A. Rankin and F. E. Wright, Am. J. Sci., **39**, p. 1; 1915; W. C. Hansen, J. Am. Ceram. Soc., **11**, p. 68; 1928.

As a dry cement raw mixture travels through the kiln, the first reactions are the liberation of the water of hydration and of carbon dioxide. The compounds, such as $3CaO.Al_2O_3$, are probably built up by the formation at first of less basic compounds, such as $CaO.Al_2O_3$ and $5CaO.3Al_2O_3$. The combination[3] of CaO with Al_2O_3, Fe_2O_3, and SiO_2 starts at temperatures around 1,000° C., and the rate of combination increases with temperature. The reactions of combination, therefore, start at about the same point in the kiln as that at which the carbon dioxide is being driven off and they proceed rapidly as the material approaches the clinkering zone. The reaction $CaO + 2CaO.SiO_2$ to form $3CaO.SiO_2$, appears to be practically completed by the time the material passes through the clinkering zone if a well-burned clinker is produced. This reaction probably is the most important and most difficult of cement manufacture. However, the combination of $CaO + 2CaO.SiO_2$ proceeds fairly rapidly in the presence of the liquid formed in Portland cement.

The influence of Al_2O_3 in producing liquid is known from the work of Rankin and Wright.[4] They found that all mixtures of $2CaO.SiO_2$ and $3CaO.SiO_2$ start to melt at 2,065° C., this being the temperature at which CaO, $2CaO.SiO_2$, and liquid coexist. The addition of $3CaO.Al_2O_3$ to mixtures of $2CaO.SiO_2$ and $3CaO.SiO_2$, lowers the temperature at which melting starts to 1,455° C.

The influence of Fe_2O_3, MgO, and Na_2O in further lowering the temperature of liquid formation has been the subject of this investigation. Microscopic and X-ray studies have been made to determine the compounds existing at equilibrium in the mixtures of CaO, Al_2O_3, SiO_2, Fe_2O_3, and MgO. At present the information available on the systems containing Na_2O is not sufficient to make it possible to determine the manner in which this oxide occurs in these mixtures or in Portland cements.

II. EXPERIMENTAL PROCEDURE

The partial chemical analyses of the raw materials used in this investigation are given below. (Table 1.)

The compositions studied are given in Table 2. A sample of about 20 g of each composition was made up by fusing,[5] in platinum, an intimate mixture of the components. These samples were powdered and used for the experiments described later.

Heating curves were made to determine the temperatures at which energy changes occurred at temperatures below 1,450° C. Charges of each of the above samples were first heated to 1,450° C. in the heating-curve furnace and cooled slowly. The charges were then reheated and the data obtained for the curves which are given later.

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[3] G. A. Rankin, Concrete, Cement Mill Section, **21**, p. 72; 1922.
[4] See footnote 2, p. 55.
[5] All fusions were made in the electric furnace described by W. C. Hansen and R. H. Bogue, Ind. Eng. Chem., **19**, p. 1260; 1927.

TABLE 1.—*Partial analyses of the raw materials used in this study*

Compound	Calcium carbonate [1]	Alumina [1]	Silica [1]	Ferric oxide [1]	Magnesia [1]	Sodium carbonate [2]	Potassium carbonate [3]
CaO	55.7	0.02	0.02	----	0.5	0.005	----
CO_2	44.1	----	----	----	----	----	----
Al_2O_3	.08	98.4	.5	----	.02	.005	----
SiO_2	----	0	99.4	----	.08	Trace.	0.0031
Fe_2O_3	.01	.10	.03	99.2	.01	.002	.0026
FeO	----	----	----	nil.	----	----	----
MgO	.01	.08	----	----	84.2	----	----
SO_3	Trace.	0	----	nil.	nil.	.005	.0001
Alkalies	.04	----	----	----	----	----	----
Cl	Trace.	.01	----	----	Trace.	.003	.0008
Loss on ignition	----	1.6	0.1	0.9	15.3	----	----

[1] By H. C. Stecker.
[2] Analysis from label, Mallinckrodt Chemical Co.
[3] Analysis from label, Baker & Adamson Chemical Co.

TABLE 2.—*Compositions of samples studied*

Sample No.	Oxide composition						Calculated compound composition				
	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	SiO_2	$3CaO.SiO_2$	$3CaO.Al_2O_3$	$2CaO.SiO_2$	MgO	$4CaO.Al_2O_3.Fe_2O_3$
1	69.5	6.8	----	----	----	23.7	57	18	25	----	----
2	66.8	15.8	----	----	----	18.0	29	42	29	----	----
3	65.7	6.5	----	5.3	----	22.5	53	17	25	5.3	----
4	67.3	6.5	----	5.3	----	20.9	71	17	6	5.3	----
5	69.2	6.6	3.3	----	----	20.9	72	12	6	----	10
6	67.1	6.6	3.3	----	----	23.0	49	12	29	----	10
7	65.6	6.3	3.1	5.2	----	19.8	70	11	4	5.2	9
8	63.6	6.3	3.1	5.2	----	21.8	47	11	27	5.2	9
9	67.9	6.6	----	----	2.2	20.9	----	----	----	----	----
10	64.3	6.3	----	5.3	2.1	22.0	----	----	----	----	----
11	65.7	6.4	3.2	----	2.2	22.5	----	----	----	----	----
12	62.3	6.1	3.1	5.1	2.1	21.3	----	----	----	----	----

Heating curves show the temperatures at which energy changes occur in a system; they, however, do not furnish any information regarding the nature of that change. The nature of the energy changes indicated by the heating curves in this study was determined by microscopic examination of charges quenched from temperatures above and below that at which the change occurred. Samples for these quenchings were prepared by reheating small charges of the 20 g samples, in a small electric furnace, to 1,450° C., and allowing them to cool slowly to establish equilibrium and complete the crystallization. They were then powdered and used for the quenching experiments which are given under the discussion of each system.

The phases present in these crystallized and quenched charges were determined by microscopic examination with a petrographic microscope. The immersion method for index of refraction deter-

minations was used. In some cases X-ray diffraction patterns were obtained to verify the results of the microscopic examination. The indices of refraction of the compounds encountered in this study are given in Table 3.

TABLE 3.—*Indices of refraction of the compounds encountered in this study*

Compound	Indices of refraction			Reference
	α	β	γ	
CaO	Isotropic.		1.832	Shepherd, Rankin, and Wright, Am. J. Sci., **28**, p. 293; 1909.
MgO	Isotropic.		1.737	
$2CaO.SiO_2$	1.717	1.726	1.735	Rankin and Wright, Am. J. Sci., **39**, p. 74; 1915.
$3CaO.SiO_2$	Mean index.[1]	1.715		
$3CaO.Al_2O_3$	Isotropic.		1.710	
$4CaO.Al_2O_3.Fe_2O_3$	1.96	2.01	2.04	Hansen, Brownmiller, and Bogue, J. Am. Chem. Soc., **50**, p. 396; 1928.

[1] Low double refraction about 0.005.

The positive microscopic identification of small amounts of $3CaO.Al_2O_3$ in the presence of large amounts of $3CaO.SiO_2$ is difficult in these complex systems. Fortunately the X-ray diffraction pattern [6] of $3CaO.Al_2O_3$ differed markedly from the X-ray diffraction patterns of the other compounds found in these preparations. It was possible, therefore, by means of X-ray diffraction patterns, to identify positively $3CaO.Al_2O_3$ in all of the completely crystallized mixtures having CaO, Al_2O_3, SiO_2, Fe_2O_3, and MgO as components.

III. BEHAVIOR OF MIXTURES ON HEATING

Before proceeding with the experimental results, it may be desirable to review briefly the behavior of such oxide systems when heated at and above their fusion temperatures. This review will be based upon the part of the concentration diagram of the system $CaO\text{-}Al_2O_3$ given in Figure 1.

When the mixture *A* (fig. 1) of $5CaO.3Al_2O_3$ and $3CaO.Al_2O_3$ is heated, melting starts at 1,395° C., and the $3CaO.Al_2O_3$ disappears at this temperature. As the temperature goes above 1,395° C., the $5CaO.3Al_2O_3$ dissolves in the liquid, and the sample is melted at temperature *D*. The mixture *B* when heated also starts to melt at 1,395° C., and the $5CaO.3Al_2O_3$ disappears at this temperature. The $3CaO.Al_2O_3$ dissolves in the liquid as the heating is continued and disappears at a temperature *E* where complete melting occurs. Mixture *C*, when heated, also starts to melt at 1,395° C., and $5CaO.3Al_2O_3$ disappears at this temperature. The $3CaO.Al_2O_3$ dissolves in the liquid as the temperature rises and at point *F* the $3CaO.Al_2O_3$ which still remains reacts with the liquid to give CaO. The CaO, in turn, does not disappear until temperature *G* is reached.

The following points are brought out in this review of the melting relations in mixtures of $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$:

1. All mixtures of the two compounds begin to melt at the same temperature.

[6] X-ray diffraction patterns of these compounds are given by E. A. Harrington, Am. J. Sci., **13**, p. 467; 1927; W. C. Hansen, J. Am. Ceram. Soc., **11**, p. 68; 1928; W. C. Hansen and L. T. Brownmiller, Am. J. Sci., **15**, p. 225; 1928.

2. In certain mixtures, $5CaO.3Al_2O_3$ disappears first; in others $3CaO.Al_2O_3$ disappears first.

3. In certain mixtures $3CaO.Al_2O_3$ disappears by dissolving in the liquid, in others it disappears partially by dissolving and partially by dissociating into solid CaO and liquid.

Another type of dissociation which is not brought out in a study of the system $CaO–Al_2O_3$ is the dissociation of a compound into two

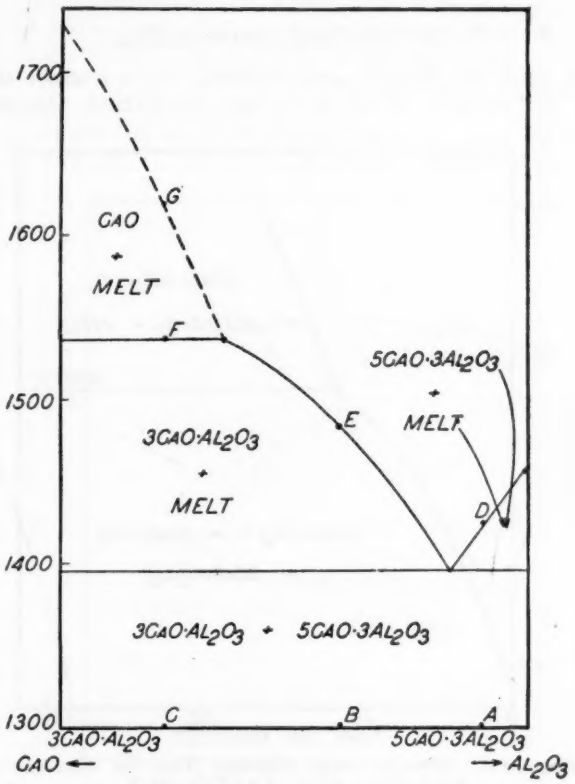

FIGURE 1.—*Portion of the temperature-concentration diagram of the system* $CaO-Al_2O_3$

solid phases without the formation of liquid. Such a dissociation occurs in the system $CaO–SiO_2$ wherein $3CaO.SiO_2$ dissociates into two solids, CaO and $2CaO.SiO_2$ before any liquid is formed in the mixture.

In a 5-component system, five compounds can coexist at equilibrium with liquid and vapor. The relations to be encountered in such a system will be similar to those found in the 2-component systems reviewed above and are as follows:

1. One or more of the compounds may dissociate into other solid phases at a temperature below that at which liquid is formed.

2. All mixtures of the five compounds will start to melt at the same temperature.

3. There will be, for each compound which does not dissociate before melting begins, a certain range of composition in which it is the first to disappear when liquid is produced in the mixture.

4. Any one of the compounds may disappear by dissociating into other solid compounds, by dissociation into a solid and liquid, or by dissolving in the liquid.

IV. EXPERIMENTAL RESULTS

1. THE SYSTEM CaO-Al_2O_3-SiO_2

From the work of Rankin and Wright,[7] it is known that in all mixtures of $3CaO.SiO_2$, $3CaO.Al_2O_3$ and $2CaO.SiO_2$ the first liquid

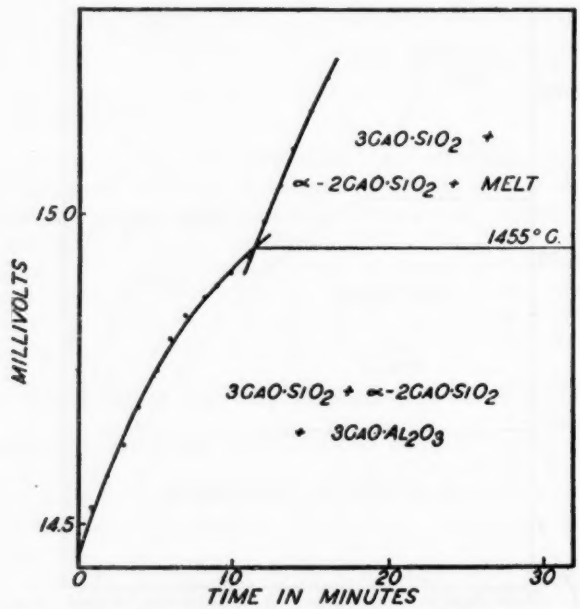

FIGURE 2.—*Heating curve diagram from the mixture: CaO, 69.5; Al_2O_3, 6.8; SiO_2, 23.7*

forms at 1,455° C. For the sake of comparison with the other systems two heating-curve diagrams are given here for mixtures in this system. The compositions in terms of the oxides and of the equilibrium compounds are given in Table 2.

Figure 2 shows that an energy change occurs in this system at 1,455° C. Quenchings were made from 1,450° and 1,460° C. The charge quenched from 1,450° C. showed no sign of melting and consisted of $3CaO.SiO_2$, $2CaO.SiO_2$, and $3CaO.Al_2O_3$. The charge quenched from 1,460° C., showed that melting had started, and the charge consisted of glass, $3CaO.SiO_2$, and $2CaO.SiO_2$. Melting, therefore, begins in this mixture at 1,455° C., and $3CaO.Al_2O_3$ disappears at this temperature.

Figure 3 is the heating curve obtained from a mixture of the composition $8CaO+Al_2O_3+2SiO_2$. Quenchings made from 1,450° and

[7] See footnote 2, p. 55.

1,460° C. showed that melting begins at 1,455° C. in this mixture, and that $3CaO.Al_2O_3$ disappears at this temperature.

2. THE SYSTEM CaO–MgO–Al_2O_3–SiO_2

Figures 4 and 5 are the heating-curve diagrams obtained from two mixtures in the system CaO–MgO–Al_2O_3–SiO_2. A charge of sample 3, Table 2, quenched from 1,370° C., consisted of $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and MgO. A charge quenched from 1,380° C. consisted of $3CaO.SiO_2$, $2CaO.SiO_2$, MgO, and glass. Melting starts in this mixture at 1,375° C., and $3CaO.Al_2O_3$ disappears at this temperature.

Figure 5 shows the same break at 1,375° C., due to the formation of liquid in sample 4, Table 2. A charge quenched from 1,380° C.

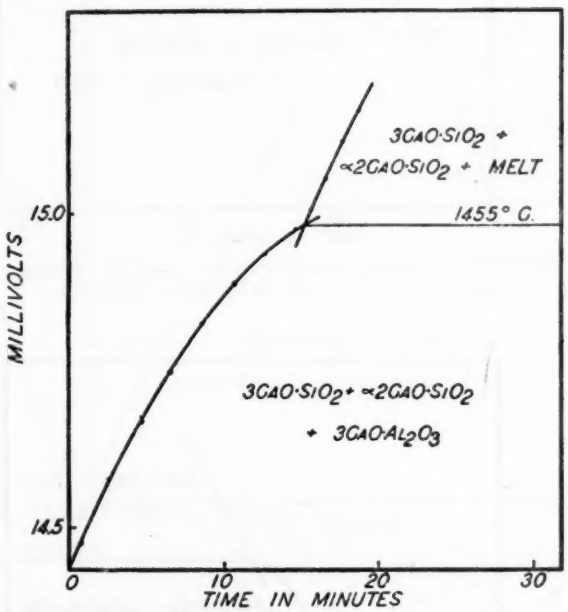

FIGURE 3.—*Heating curve diagram from the mixture: CaO, 66.8; Al_2O_3, 15.2; SiO_2, 18.0*

consisted of $3CaO.SiO_2$, $3CaO.Al_2O_3$, MgO, CaO, and glass. $2CaO.SiO_2$ disappears at 1,375° C. in this mixture, and CaO appears as a new phase. A charge quenched from 1,400° C. consisted of $3CaO.SiO_2$, CaO, MgO, and glass. $3CaO.Al_2O_3$ disappears at 1,390° C. in this sample by partially dissolving and partially dissociating forming CaO.

The $2CaO.SiO_2$ disappears at 1,375° C. in this mixture partially by dissolving and partially by reacting with $3CaO.Al_2O_3$ to form $3CaO.SiO_2$. There is not sufficient $2CaO.SiO_2$, however, to react with all of the $3CaO.Al_2O_3$, and the remaining $3CaO.Al_2O_3$ disappears at 1,390° C.

This reaction of $3CaO.Al_2O_3$ is one of importance to the cement manufacturer. The SiO_2 and Al_2O_3 of a Portland cement raw mixture can combine with a certain maximum amount of CaO. It may be

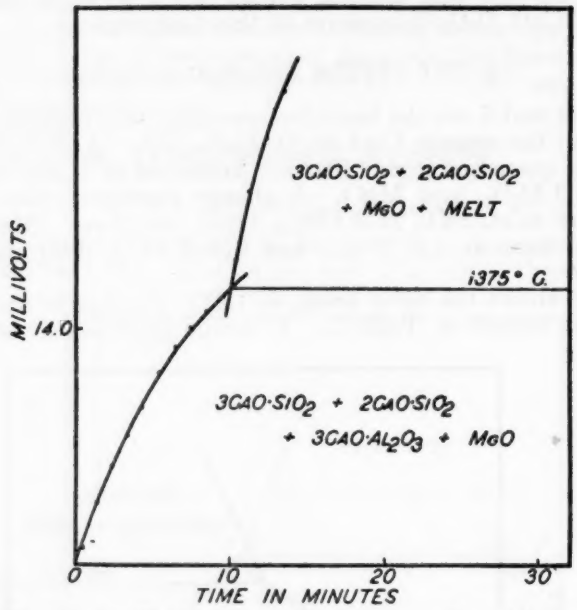

FIGURE 4.—*Heating curve diagram from the mixture: CaO, 65.7; Al_2O_3, 6.5; SiO_2, 22.5; MgO, 5.3*

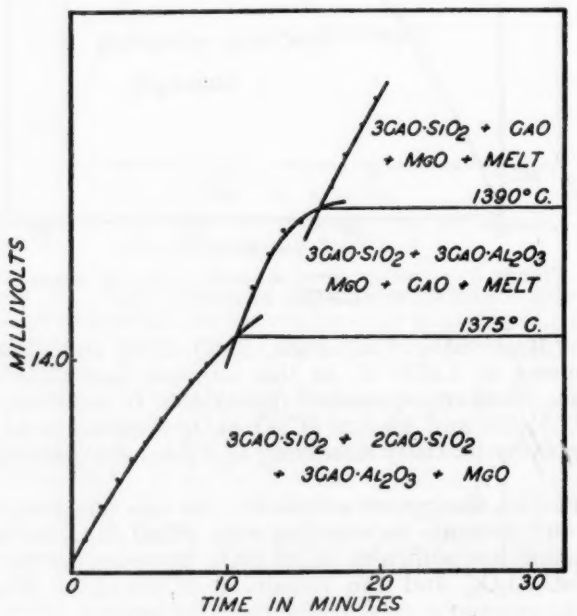

FIGURE 5.—*Heating curve diagram from the mixture: CaO, 67.3; Al_2O_3, 6.5; SiO_2, 20.9; MgO, 5.3*

difficult, however, to get this CaO into combination in practice. If such a difficulty were encountered, the most natural thing to do would be to increase the time and degree of heating. Such a procedure would not help when the uncombined CaO is due to the dissociation of $3CaO.Al_2O_3$. This CaO must be recombined during cooling, and unless the rate is such as to allow the CaO to react with the liquid and form $3CaO.Al_2O_3$, the cement will contain uncombined CaO.

3. THE SYSTEM CaO-Al_2O_3-Fe_2O_3-SiO_2

The crystalline phases formed in these mixtures, samples 5 and 6, Table 2, are $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3$.

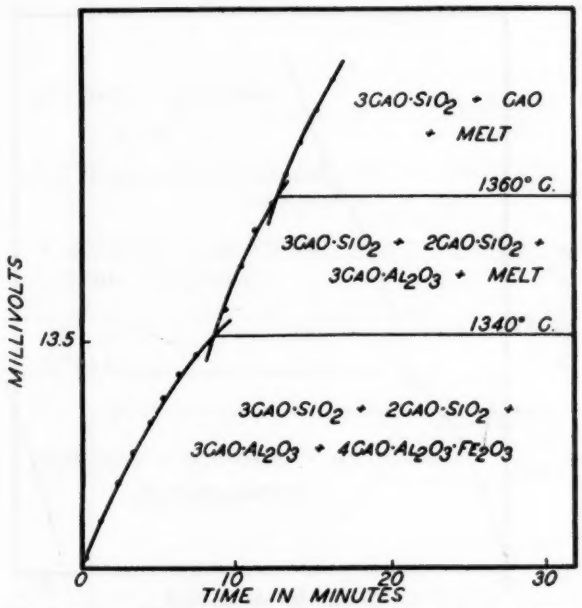

FIGURE 6.—*Heating curve diagram from the mixture: CaO, 69.2; Al_2O_3, 6.6; SiO_2, 20.9; Fe_2O_3, 3.3*

Fe_2O_3. The first three phases were easily identified, but the $4CaO.Al_2O_3.Fe_2O_3$ was present in the annealed samples as very small grains and as edges on the other grains. The optical properties of these small grains agreed with those of $4CaO.Al_2O_3.Fe_2O_3$, but to make more certain that this compound exists in equilibrium with $3CaO.SiO_2$, $2CaO.SiO_2$, and $3CaO.Al_2O_3$, a preparation of the composition CaO 56.5, Al_2O_3 19.7, SiO_2 10.5, and Fe_2O_3 13.2 per cent was made up and examined. Such a mixture at equilibrium contains by calculation 40 per cent of $4CaO.Al_2O_3.Fe_2O_3$. The $4CaO.Al_2O_3.Fe_2O_3$ was well crystallized in this preparation and was positively identified, both by microscopic and X-ray examination, together with $3CaO.SiO_2$, $2CaO.SiO_2$, and $3CaO.Al_2O_3$.

The heating curves obtained from mixtures 5 and 6 are given in Figures 6 and 7. Quenchings from 1,330° C. and 1,350° C. show that the break at 1,340° C. is due to the beginning of melting, and that

$4CaO.Al_2O_3.Fe_2O_3$ disappears at this temperature in these mixtures. At 1,360° C. in sample 5, Table 2, and at 1,365° C. in sample 6, Table 2, the $3CaO.Al_2O_3$ disappears. In sample 5, CaO appears at 1,360° C., due to the dissociation of the $3CaO.Al_2O_3$.

4. THE SYSTEM CaO-MgO-Al_2O_3-Fe_2O_3-SiO_2

Figures 8 and 9 are the heating-curve diagrams for the two mixtures, samples 7 and 8, Table 2, studied in this system. The crystalline phases in these mixtures at equilibrum are $3CaO.SiO_2$, $3CaO.Al_2O_3$, $2CaO.SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and MgO.[8] In these samples as in samples 5 and 6 the ferric-oxide containing phase was present as small

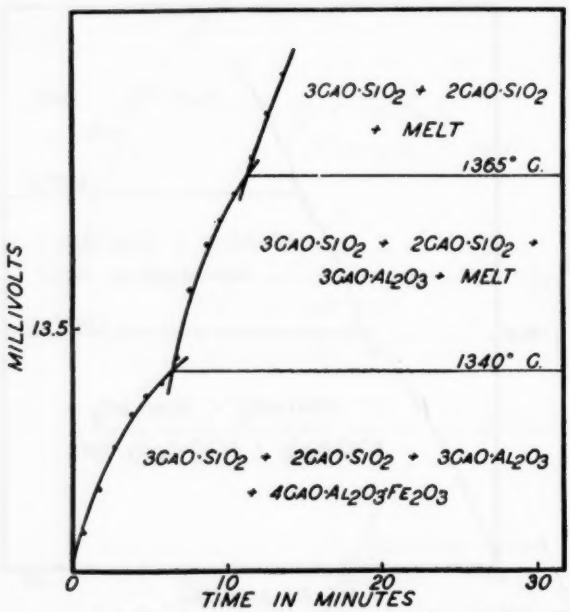

FIGURE 7.—*Heating curve diagram from the mixture: CaO, 67.1; Al_2O_3, 6.6; SiO_2, 23.0; Fe_2O_3, 3.3*

grains and as edges on the other grains. The mixture CaO 57.5, Al_2O_3 16.7, Fe_2O_3 8.4, MgO 4.3, SiO_2 13.1 was made up and studied as a further check on the ferric-oxide containing compound existing in equilibrium with $3CaO.SiO_2$, $2CaO.SiO_2$, and $3CaO.Al_2O_3$. In this mixture the $4CaO.Al_2O_3.Fe_2O_3$ was present as well-developed crystals and was identified together with the other phases listed above.

The breaks at 1,300° C. in the heating curves (figs. 8 and 9) were shown by quenching to be caused by the formation of liquid. The

[8] In a former publication (Hansen and Brownmiller, Am. J. Sci., 15, p. 225; 1928), it was reported that MgO enters into solid solution with $4CaO.Al_2O_3.Fe_2O_3$, the end member of the series being $4CaO.2MgO.Al_2O_3.Fe_2O_3$. Magnesia in excess of that required for the above combination was found to remain as uncombined MgO. More recent information obtained in this laboratory indicates that the amount of the solid solution is much smaller than had previously been reported. Although there is no reasonable doubt that a large part of the magnesia remains uncombined, the exact nature and degree of the reaction by which the $4CaO.Al_2O_3.Fe_2O_3$ is changed in color and pleochroism in the presence of a small amount of magnesia has not been determined. This problem is under further investigation. At present the magnesia may be considered as remaining essentially uncombined, and the iron compound as existing essentially in the form $4CaO.Al_2O_3.Fe_2O_3$.

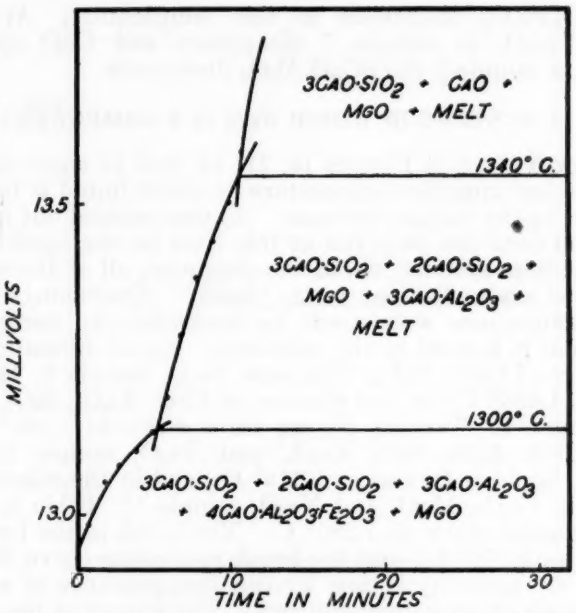

FIGURE 8.—*Heating curve diagram from the mixture: CaO, 65.6; Al_2O_3, 6.3; SiO_2, 19.8; Fe_2O_3, 3.1; MgO, 5.2*

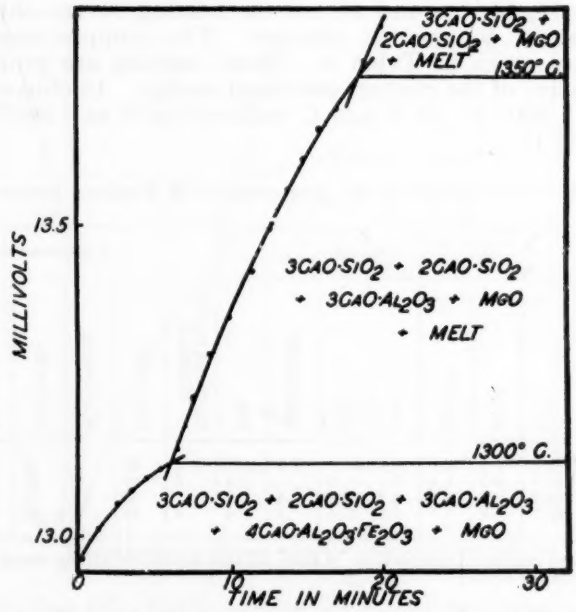

FIGURE 9.—*Heating curve diagram from the mixture: CaO, 63.6; Al_2O_3, 6.3; SiO_2, 21.8; Fe_2O_3, 3.1; MgO, 5.2*

$4CaO.Al_2O_3.Fe_2O_3$ disappears at this temperature. At 1,340° C. the $3CaO.Al_2O_3$ in sample 7 disappears and CaO appears. At 1,350° C. in sample 8 the $3CaO.Al_2O_3$ disappears.

5. SYSTEMS IN WHICH Na_2O IS A COMPONENT

The curves given in Figures 10, 11, 12, and 13 show the influence of Na_2O in lowering the temperature at which liquid is formed when it is added to the various systems. As was pointed out in the introduction, no data can be given at this time on the equilibrium compounds in these systems, so, in the diagrams, all of the solid phases are grouped under the one term, "solid." Quenchings and microscopic examinations were made to determine the temperatures at which liquid is formed in the mixtures. Liquid formation starts in the mixture of CaO, Al_2O_3, SiO_2, and Na_2O, sample 9, Table 2, Figure 10, at 1,430° C.; in the mixture of CaO, Al_2O_3, SiO_2, MgO, and Na_2O, sample 10, Table 2, Figure 11, it starts at 1,365° C.; in the mixture CaO, Al_2O_3, SiO_2, Fe_2O_3, and Na_2O, sample 11, Table 2, Figure 12, liquid is formed at 1,315° C.; and in the mixture of CaO, Al_2O_3, SiO_2, Fe_2O_3, MgO, and Na_2O, sample 12, Table 2, Figure 12, liquid formation starts at 1,280° C. The break in the heating curve Figure 12 at 1,370° C., and the break in heating curve Figure 13 at 1,315° C. are probably caused by the disappearance of a crystalline phase at each of these temperatures. The nature of the phases disappearing at these temperatures was not determined.

6. COMMERCIAL PORTLAND CEMENT CLINKERS

Figures 14, 15, 16, and 17 are the heating curves obtained from four different commercial clinkers. The compositions of these clinkers are given in Table 4. These samples are probably fairly representative of the clinkers produced to-day. In clinker A melting begins at 1,300° C., in B and C melting starts at 1.290° C., and in D at 1,298° C.

TABLE 4.—*Compositions of the four commercial Portland cement clinkers* [1]

Sample	Analyses								Compound composition					
	CaO	Al_2O_3	Fe_2O_3	MgO	SiO_2	Ignition loss	SO_3	Na_2O and K_2O by difference	$3CaO.SiO_2$	$3CaO.Al_2O_3$	$2CaO.SiO_2$	MgO	$4CaO.Al_2O_3.Fe_2O_3$	$CaSO_4$
A	66.0	4.9	4.6	0.8	21.9	1.4	------	0.4	63	5	15	0.8	14	------
B	63.0	6.3	4.4	3.4	21.9	------	0.3	.7	40	9	33	3.4	13	0.5
C	64.7	7.5	2.9	4.2	20.4	.4	.3	------	53	15	18	4.2	9	.5
D	64.7	5.9	4.1	1.8	22.4	.1	.6	.4	46	9	30	1.8	12	1.0

[1] The calculated compound compositions of these clinkers neglect everything except the CaO, Al_2O_3, Fe_2O_3, MgO, SiO_2, and SO_3.

Dyckerhoff [9] gives a heating curve obtained from a German Portland cement clinker produced in his laboratory from commercial raw materials in which the first break appears at 1,285° C.

[9] Dissertation, University of Frankfurt; 1925.

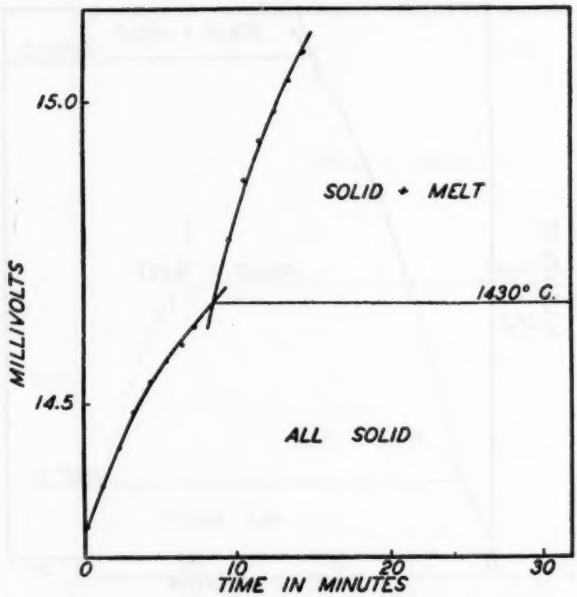

FIGURE 10.—*Heating curve diagram from the mixture: CaO, 67.9; Al_2O_3, 6.6; SiO_2, 20.9; Na_2O, 2.2*

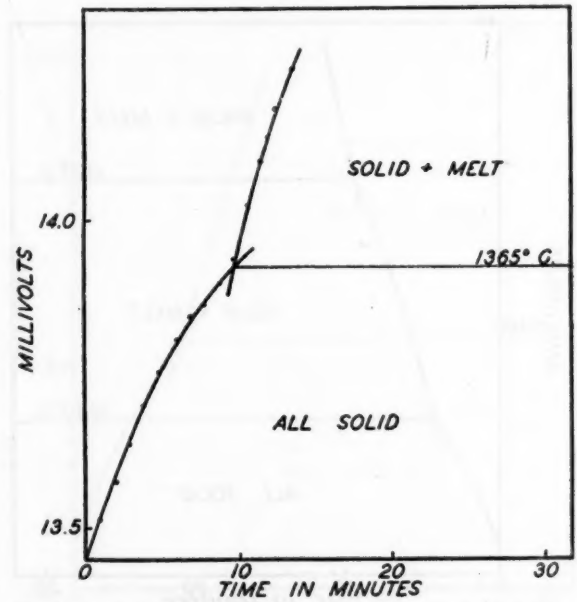

FIGURE 11.—*Heating curve diagram from the mixture: CaO, 64.3; Al_2O_3, 6.3; SiO_2, 22.0; MgO, 5.3; Na_2O, 2.1*

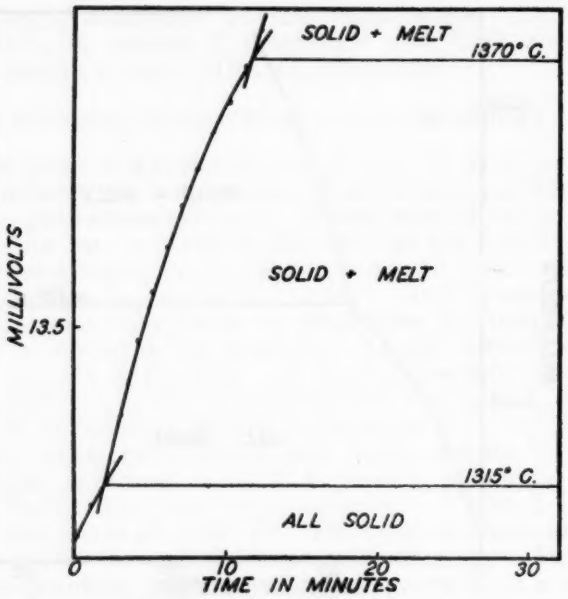

FIGURE 12.—*Heating curve diagram from the mixture: CaO, 65.7; Al_2O_3, 6.4; SiO_2, 22.5; Fe_2O_3, 3.2; Na_2O, 2.2*

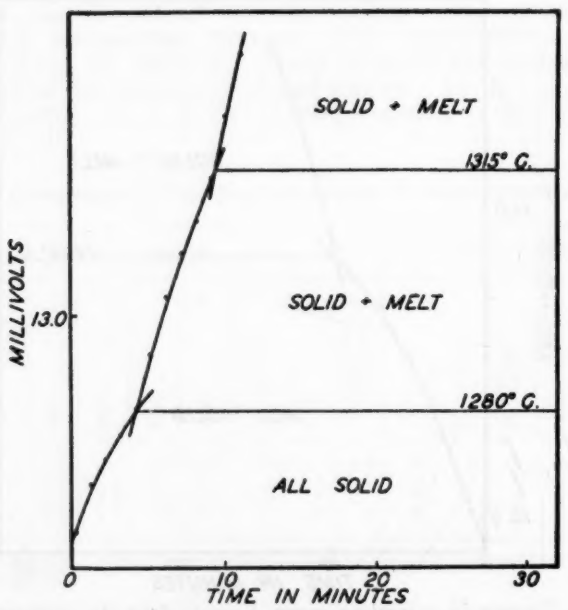

FIGURE 13.—*Heating curve diagram from the mixture: CaO, 62.3; Al_2O_3, 6.1; SiO_2, 21.3; Fe_2O_3, 3.1; MgO, 5.1; Na_2O, 2.1*

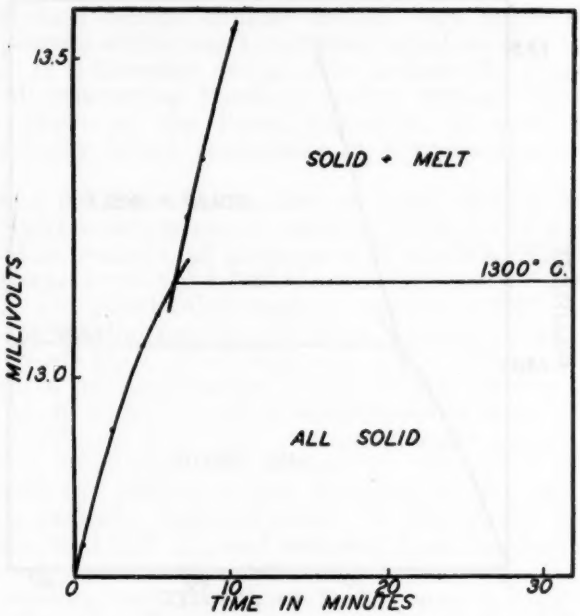

FIGURE 14.—*Heating curve diagram from a commercial Portland cement clinker A*

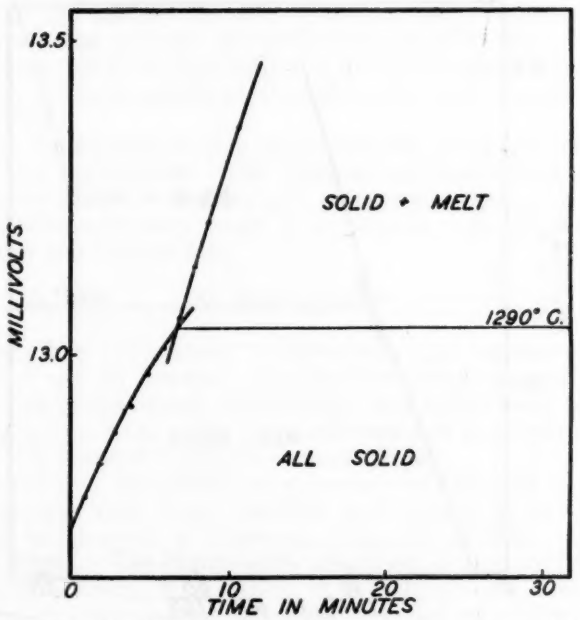

FIGURE 15.—*Heating curve diagram from a commercial Portland cement clinker B*

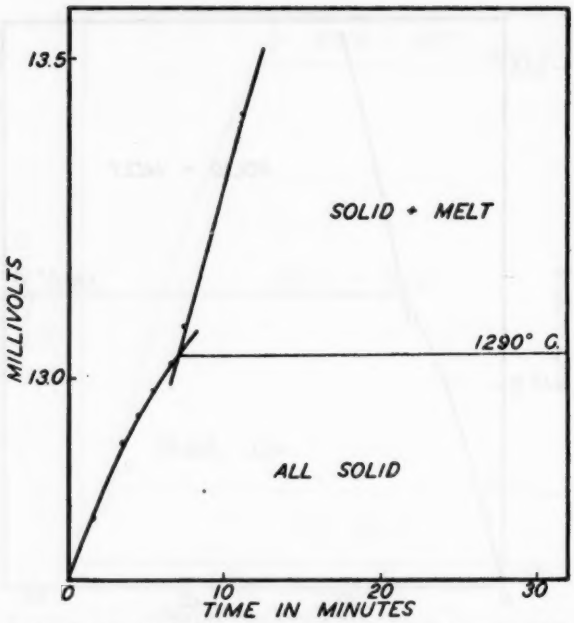

FIGURE 16.—*Heating curve diagram from a commercial Portland cement clinker C*

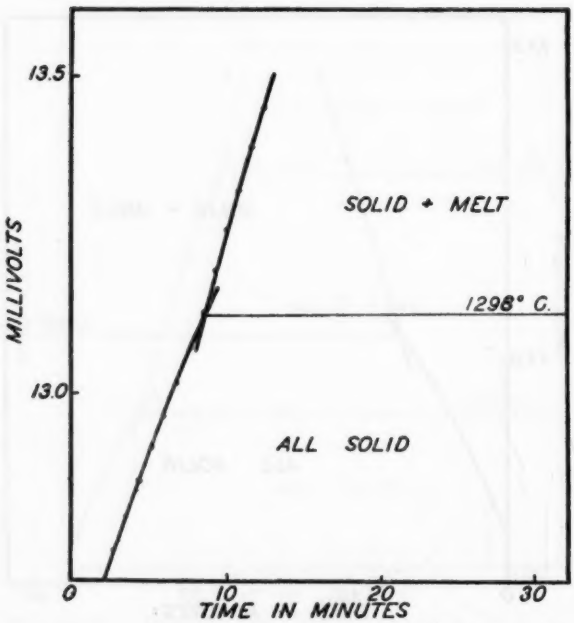

FIGURE 17.—*Heating curve diagram from a commercial Portland cement clinker D*

Some Portland cement clinkers contain very minor amounts of other components which may lower their initial melting temperature somewhat. It is therefore not possible to draw the general conclusion that all commercial Portland cement clinkers will behave as these do. However, the liquid formation in most commercial clinkers probably is not appreciable at temperatures much below 1,290° C.

There may be a certain amount of liquid formed in Portland cement clinkers which is not in equilibrium with the final reaction products. For example, all mixtures of $3CaO.SiO_2$, $2CaO.SiO_2$, and $3CaO.Al_2O_3$ start to melt at 1,455° C.; and all mixtures [10] of $2CaO.SiO_3$, $3CaO.Al_2O_3$, and $5CaO.3Al_2O_3$ begin to melt at 1,335° C. Samples 1 and 2, Table 2, after first heating might contain some $5CaO.3Al_2O_2$ as well as $3CaO.Al_2O_3$, $2CaO.SiO_2$, and CaO. When the temperature of such a mixture reached 1,335° C. the eutectic mixture of $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$, and $2CaO.SiO_2$ would melt. This liquid is not in equilibrium with CaO and would react immediately with CaO to form $3CaO.Al_2O_3$ and $3CaO.SiO_2$. If such a sample were removed from the furnace at this temperature the material would appear as a partially clinkered mass. If this clinker were ground and reheated to 1,350° C., and removed from the furnace at this temperature, it would not be clinkered.

Similar melting may take place in the more complex Portland cement mixtures, so that a certain amount of clinkering may be effected in practice at a temperature below that at which the liquid in equilibrium with the final reaction products is formed. Such melting would not take place if the raw mixture were sufficiently fine and uniform and if the rate of heating did not exceed that required to keep the mixture at equilibrium at all times. This study, therefore, does not show definitely the temperatures at which clinkering of these mixtures might start, unless the above ideal conditions are maintained.

It may be stated that in this paper only the temperatures of liquid formation are considered. The amount of liquid present at any given temperature, its viscosity and other properties, will vary with the composition and may exert a significant influence on the rate of reaction in the cement kiln.

V. SUMMARY

1. A study has been made to determine the influence of Fe_2O_3, MgO, and Na_2O in lowering the temperatures at which melting starts when they are added individually and collectively to mixtures of CaO, Al_2O_3, and SiO_2. The mixtures used had compositions similar to those of commercial Portland cement clinker.

2. The results of this study are summarized in Table 5.

3. Microscopic and X-ray studies were made to determine the equilibrium compounds of cements composed of CaO, Al_2O_3, SiO_2, Fe_2O_3, and MgO. The compounds identified in these mixtures were $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, and MgO.

[10] See footnote 3, p. 56.

TABLE 5.—*Table showing the temperatures at which melting starts when Al_2O_3, Fe_2O_3, MgO, and Na_2O are added to mixtures of CaO and SiO_2 in the proportions found in Portland cement*

Systems	Compositions studied	Temperatures at which melting starts
		°C.
CaO, SiO_2	Rankin and Wright Am. J. Sci., **39**, p. 1, 1915.	2,065
CaO, SiO_2, Al_2O_3	Samples 1 and 2	1,455
CaO, SiO_2, Al_2O_3, Na_2O	Sample 9	1,430
CaO, SiO_2, Al_2O_3, MgO	Samples 3 and 4	1,375
CaO, SiO_2, Al_2O_3, Fe_2O_3	Samples 5 and 6	1,340
CaO, SiO_2, Al_2O_3, Na_2O, MgO	Sample 10	1,365
CaO, SiO_2, Al_2O_3, Na_2O, Fe_2O_3	Sample 11	1,315
CaO, SiO_2, Al_2O_3, MgO, Fe_2O_3	Samples 7 and 8	1,300
CaO, SiO_2, Al_2O_3, Na_2O, MgO, Fe_2O_3	Sample 12	1,280

VI. ACKNOWLEDGMENT

The X-ray studies referred to in this paper were made by L. T. Brownmiller. The author takes pleasure in expressing his appreciation to him for this assistance.

WASHINGTON, January 7, 1929.

NOTES ON THE DESIGN OF 4-TERMINAL RESISTANCE STANDARDS FOR ALTERNATING CURRENTS

By Francis B. Silsbee

ABSTRACT

The design of a resistance standard for use with alternating current involves not only the consideration of the value, definiteness, and permanence of the resistance and the adequate cooling of the metal parts, which are encountered in direct-current standards as well, but also the consideration of the inductance and of the possible change in the resistance of the standard with the frequency of the current flowing in it. These notes give the theoretical basis for the computation of the inductance of resistance standards which consist of a system of straight conductors long in comparison to their diameters. Most standards used in the measurement of large currents are of this type. Formulas are given for the skin effect in various combinations of flat strips and coaxial tubes. Methods of attaching and locating the potential leads so as to minimize the possibility of error from stray magnetic fields and yet permit of convenient adjustment of the resistance are discussed. As examples of the principles here set forth, detailed descriptions are given of two groups of resistance standards which have been constructed at the Bureau of Standards for testing current transformers. These standards range in resistance from 0.05 to 0.0002 ohm and in current capacity from 10 to 2,500 amperes.

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I. INTRODUCTION

The constantly increasing use of electrical energy in large amounts has given more and more importance to the problem of accurately measuring alternating currents of large value. Such measurements usually involve the use of a current transformer, the secondary winding of which serves to supply to the measuring instruments proper a current of convenient amount, which bears a definite relation in magnitude and phase to the much larger current flowing in the primary winding. The exact determination of the relation of secondary to primary currents must be determined by suitable measurements, which in most cases directly or indirectly require the use of resistance standards or "shunts"[1] which are capable of carrying the primary current and which have definite and accurately known resistance and inductance.

The Bureau of Standards has given considerable attention to the design of such resistance standards, and Scientific Paper [2] No. 281,

[1] In this paper the term "shunt" will be used in place of the inconvenient though, perhaps, more nearly correct phrase "4-terminal resistance standard."

[2] B. S. Bull. 13, p. 375.

published in 1916, describes the results of our earlier work on this subject. The purpose of the present paper is to supplement the earlier one (*a*) by presenting the basis for the theoretical computation of inductance from a somewhat different point of view, (*b*) by reporting the results of further experimental work bearing on some possible sources of error in such measurements, and (*c*) by describing a series of shunts of two different types which have been constructed at the bureau in recent years.

The computation of the inductance of systems of conductors having various geometrical configurations is useful in a number of applications. One of these is to determine with high precision the inductance of shunts which are to be used primarily as standards of inductance with which other shunts are to be compared. It often happens, however, that considerations of convenience or adjustability require that a working standard of resistance have a shape which departs considerably from any of those for which it is feasible to carry through an exact mathematical calculation of inductance. Such shunts must be regarded as secondary standards and for precise work must be compared experimentally with primary inductance standards. Nevertheless, it is frequently desirable to be able to estimate roughly the inductance to be expected with such a type of construction, and the procedure given below may in many cases be applied to give such results with sufficient accuracy for the purpose at hand.

In the following pages will be found a derivation of the geometric mean distance formula on which the inductance computations are based with instructions for applying this to conductors of various types. A discussion of the extent to which conditions in an actual standard may depart from the ideal as the result of skin effect, end effect, attachment of potential leads, etc., is then given. It is then shown how these principles can be applied to the design of a new type of air-cooled flat-strip shunt; and a brief description is given of some tubular oil-cooled shunts recently completed.

II. THEORETICAL BASIS FOR CALCULATION OF INDUCTANCE

A general definition of the inductance of a 4-terminal resistor is obtained by considering that a sinusoidal alternating current I flows through the resistor from terminal 1 to terminal 2, and that an alternating electromotive force E then appears[3] between terminals 3 and 4. If the vector ratio of E to I is given by

$$\frac{E}{I}=Z=R'+j\,\omega\,L \tag{1}$$

where $\omega=2\,\pi\times$ frequency; then L is the inductance of the resistor, and R' is its alternating-current resistance. The conditions which must be satisfied to make L a definite quantity are discussed at length elsewhere;[4] but the principal requirements are that the potential terminals 3 and 4 shall be located at a considerable distance from the current terminals 1 and 2, and that the two terminals of each pair shall be as close together as possible.

[3] See Section IX for meaning of the symbols used in this paper.
[4] Wenner, B. S. Bull., 8, p. 577; 1912; B. S. Sci. Paper No. 181.

In considering problems involving the characteristics of 4-terminal resistors, two very general principles are often of great value. The first of these is the "reciprocal theorem"[5] which states that if current is passed through terminals 3 and 4 and the resulting electromotive force is observed at terminals 1 and 2 the resistance and inductance will have the same numerical values as if the converse choice of terminals had been made and the electromotive force had been observed at 3 and 4 when current was passing through 1 and 2. This theorem is exceedingly convenient in discussing the inductance of complicated groups of conductors, since that pair of terminals can be considered as current terminals which yields the simplest set of streamlines and equipotential surfaces.

The second useful conception is that of regarding the two possible current paths (that through 1 and 2 and that through 3 and 4) as separate and distinct circuits, which can be called the "current circuit" and the "potential circuit," respectively. The self-inductance of the complete resistor then becomes the same as the mutual inductance between the two circuits so visualized. The fact that throughout part of their volumes the two circuits coincide in space does not affect the argument. When regarded as a mutual inductance, it is easier to see that the total inductance is the algebraic sum of the mutual actions of the several parts of the one circuit upon those of the other. The effect of an external stray field on the resistor can be considered as a mutual inductance between the potential circuit and the circuit which produces the external field.

Most shunts intended for use with alternating currents approximate more or less closely to an ideal configuration of conductors, for which the mathematical process of summing up the mutually inductive effects of each part of the current circuit on each part of the potential circuit can be carried through with comparative ease. The accuracy with which the actual inductance of the shunt agrees with the inductance computed for the ideal configuration depends, of course, on the fidelity with which the actual construction approaches the ideal configuration. The configuration approximated in the design of many alternating current shunts is that of a group of infinitely long parallel straight conductors of uniform cross section and of homogeneous, isotropic material. In any conductor of such a group, the streamlines of current are necessarily straight and parallel to the bounding surfaces of the conductor, and the potential gradient has a constant value at all points of any one conductor, both along its length and over its cross section. If the frequency is sufficiently low, the current density will also be uniform over the cross section. The inductance formulas given in this (and in most other papers) are based on this assumption of uniform current distribution.

Numerical computations of the inductance of systems of straight parallel conductors can most readily be based upon the following derivation [6] of the mutual inductance between two circuits of this type.

Figure 1 shows the cross section of four such conductors. Consider that conductors 1 and 2 of area S_1 and S_2 form the outgoing

[5] Kirchhoff, Pogg. Ann., **72**, 1847.

[6] The derivation here given closely follows the presentation in Orlich's "Kapazität und Induktivität," p. 68, F. Vieweg u. Sohn, Leipzig; 1909.

and return conductors of a single circuit which carries a current I_p. Similarly, consider that conductors 3 and 4 of areas S_3 and S_4 constitute a second circuit which carries a current I_s. If i_1, i_2, i_3, and i_4 are the current densities in conductors 1, 2, 3, and 4, respectively, counted positive when in the same direction in all conductors, and

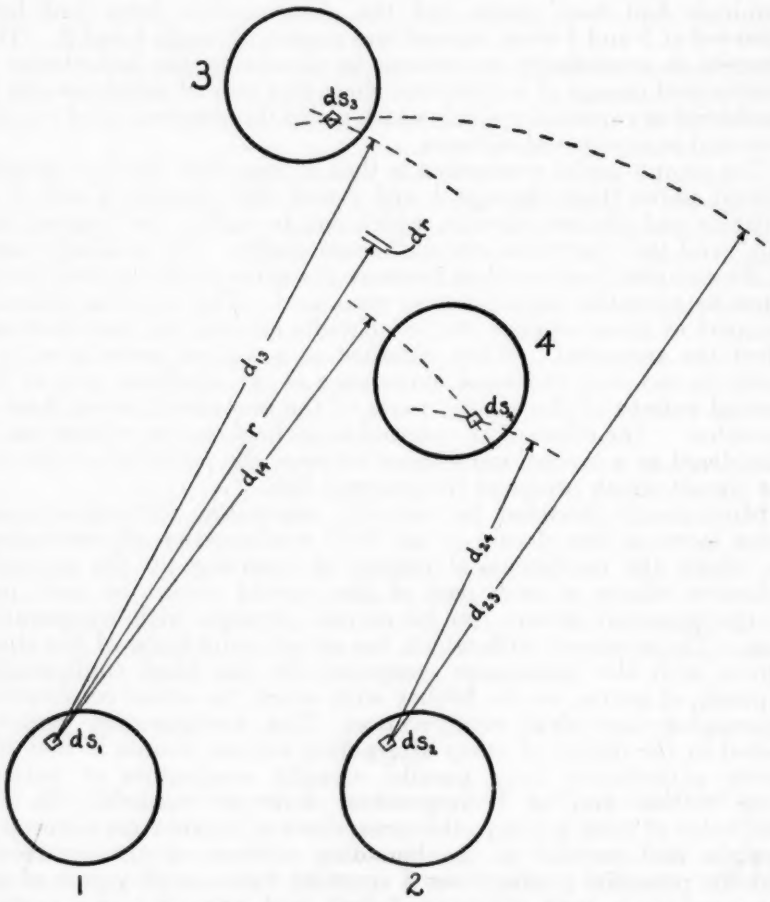

FIGURE 1.—*Cross section of four long straight conductors illustrating calculation of mutual inductance*

the currents are uniformly distributed over the cross sections of the conductors

$$i_1 S_1 = -i_2 S_2 = I_p$$

and (2)

$$i_3 S_3 = -i_4 S_4 = I_s$$

Consider each conductor divided into a number of infinitesimal filaments, their cross sections dS_1, dS_2, dS_3, and dS_4 being so chosen that the current $i_2 dS_2$ in a filament of conductor 2 may be considered as the return of the current element $i_1 dS_1$ in conductor 1, and similarly for conductors 3 and 4.

Now, the flux for a length l of circuit, due to the current in filament dS_1 linking the circuit formed by dS_3 and dS_4 is

$$l\int_{d_{13}}^{d_{14}}\frac{2i_1 dS_1}{r}dr = 2i_1 l dS_1\,(\log_e d_{14} - \log_e d_{13}) \tag{3}$$

where r is a radial distance from dS_1.

d_{13} and d_{14} are the distances from dS_1 to dS_3 and dS_4, respectively.

The corresponding number of flux linkages due to the current in dS_2 is similarly

$$2i_2 l dS_2\,(\log_e d_{24} - \log_e d_{23})$$

The mutual magnetic energy corresponding to these linkages is obtained by multiplying the total number of linkages by the element of current $i_3 dS_3 = -i_4 dS_4$ which is linked with it. This magnetic energy is therefore

$$\begin{aligned} dW = 2l\,[&i_1 dS_1\,(-i_4 dS_4 \log_e d_{14} - i_3 dS_3 \log_e d_{13}) + i_2 dS_2\,(-i_4 dS_4 \log_e d_{24} \\ &- i_3 dS_3 \log_e d_{23})] \end{aligned} \tag{4}$$

On substituting for the various current densities their value in terms of the total currents from equation (2) this becomes

$$\begin{aligned} dW = 2l I_p I_s \Big[&\frac{1}{S_1 S_4}\log_e d_{14} dS_1 dS_4 - \frac{1}{S_1 S_3}\log_e d_{13} dS_1 dS_3 \\ &- \frac{1}{S_2 S_4}\log_e d_{24} dS_2 dS_4 + \frac{1}{S_2 S_3}\log_e d_{23} dS_2 dS_3\Big] \end{aligned} \tag{5}$$

The total mutual magnetic energy is obtained by adding all these elementary contributions—that is, by integrating over the cross sections of the conductors. This total energy can also be expressed in terms of the mutual inductance M of the two circuits as

$$W = M I_p I_s \tag{6}$$

Combining equations (5) and (6) and indicating the integrations gives

$$\begin{aligned} M = 2d\Big[&\frac{1}{S_1 S_4}\int_{S_1}\int_{S_4}\log_e d_{14} dS_1 dS_4 - \frac{1}{S_1 S_3}\int_{S_1}\int_{S_3}\log_e d_{13} dS_1 dS_3 \\ &- \frac{1}{S_2 S_4}\int_{S_2}\int_{S_4}\log_e d_{24} dS_2 dS_4 + \frac{1}{S_2 S_3}\int_{S_2}\int_{S_3}\log_e d_{23} dS_2 dS_3\Big] \end{aligned} \tag{7}$$

Now, the definition of the geometric mean distance D_{xy} between two areas S_x and S_y is

$$\log_e D_{xy} = \frac{1}{S_x S_y}\int_{S_x}\int_{S_y}\log_e d_{xy}\, dS_x\, dS_y \tag{8}$$

and also the mutual inductance is defined as the ratio of secondary flux linkages to primary current, so that

$$M = \frac{\phi}{I} = 2l\,[\log_e D_{14} - \log_e D_{13} - \log_e D_{24} + \log_e D_{23}] \tag{9}$$

or

$$= 2\,l \log_e \frac{D_{14}\,D_{23}}{D_{13}\,D_{24}}$$

In the foregoing linkages have been counted as positive when due to the current in 1 and when threading circuit 3 and 4 in the same direction as if due to a current in 3 which is in the same direction as the current in 1. The sign of M as given by equation (9) is therefore such that if conductors 2 and 3 were joined and a current sent from 1 to 4 through the series circuit thus formed the total self-inductance would be given by

$$L = L_{12} + L_{34} + 2\ M_{12.34} \tag{10}$$

If we wish to pass from the mutual inductance of two separate circuits to the self-inductance of a 4-terminal resistor, one or more of the conductors of the potential circuit must be considered as coinciding with the corresponding conductor of the current circuit. Thus, the self-inductance of the circuit formed by the two conductors 1 and 2 only, is obtained if we imagine conductor 3 to coincide with 1 and 4 with 2. Equation (9) then becomes

$$L = 2l \log_e \frac{D^2_{12}}{D_{11}\, D_{12}} \tag{11}$$

where the symbol D_{11} indicates the geometric mean distance of the cross section of conductor 1 from itself.

In case conductors 1 and 2 are equal, equation (11) reduces to the usual formula.

$$L = 4l \log_e \frac{D_{12}}{D_{11}} \tag{12}$$

An actual resistance standard will unavoidably depart from the ideal configuration in a number of respects. The departure from the condition of infinite length is discussed below in the section on "end effects," and the departure from uniform current distribution in the section on "skin effect." Effects arising from local inhomogeneities in the conductivity of the metal are, of course, not amenable to mathematical treatment. In certain cases, however, such as concentric tubular shunts, the existence of any resulting irregularity in current distribution can be detected by sending an alternating current through the shunt and exploring the magnetic field with a search coil connected to a vibration galvanometer. Any departure from straightness is usually entirely negligible. In fact, the formulas deduced on the basis of the foregoing assumptions of long straight conductors may sometimes be applied with fairly good approximation to cases when the entire system of conductors is curved, provided only that the radius of curvature is large compared with the transverse dimensions of the conductors.

The proper sign for inductance can be obtained by applying the following procedure to a sketch of the system. Starting at one current terminal proceed along the current circuit, indicating by an arrow on each conductor an assumed direction of continuous current flow. Indicate by similar arrows on each conductor of the potential circuit such a direction that on the common conductors the arrows of the two sets have the same direction. Assign a number to each conductor in such a way that all conductors marked with arrows in one direction have odd numbers and those marked oppositely have

even numbers. Group the conductors of each circuit into pairs so that the two members of each pair are marked with arrows pointing in opposite directions, and so that no conductor is assigned to more than one pair in the same current or potential circuit. If either or both circuits have an odd number of conductors, either (*a*) the corresponding terminals are separated by the length of the resistor and its inductance is indefinite until the location of the return conductor is specified (for example, an ordinary resistance standard for direct current) or (*b*) the terminals are close together as a result of the entire system being curved to a radius large compared with the transverse dimensions of the conductors (for example, the L. and N. adjustable secondary resistor). In this latter case the circuits having the odd number of conductors should be considered as having an additional conductor located at a great distance from the others, but serving to complete it. The geometric mean distances of this imaginary conductor from the members of each pair of conductors in the other circuit will always appear in equation (9) in such a way as to cancel each other.

For each pair of conductors in the current circuit combined with each pair of conductors in the voltage circuit compute a contribution to the total inductance by equation (9). The algebraic sum of these contributions is then the desired inductance. When substituting in equation (9) distances having like subscripts (that is, both even or both odd) must be in the denominator and those having unlike subscripts in the numerator.

The conductor cross sections used in resistance standards are almost invariably either rectangles or circular annuli or special cases of these, such as lines (for thin strips) or circles (round wires). The derivation of the formulas for the geometric mean distance between such shapes from the definition of G. M. D. is not difficult but is rather laborious in the case of the rectangles. In the case of the circular shapes the evaluation of the definite integral [7] which represents the geometric mean distance is given by the formula.

$$\int_0^{\pi} \log_e (k \pm t \cos y)\, dy = \pi \log_e \left(\frac{k + \sqrt{k^2 - t^2}}{2} \right); \; k \geqq t) \qquad (12)$$

Bureau of Standards Scientific Paper [8] No. 169 on pages 168 to 170 gives all the exact expressions for circular and annular G. M. D's.

In the case of thin-walled tubes the formulas can be much simplified.[9] Scientific Papers No. 281, page 400, and No. 320, page 565, also give the simplified expressions for the inductance of shunts using several possible combinations of tubes.

The most general formula for the G. M. D. of rectangles placed obliquely but with their sides parallel, is given by Gray,[10] but with certain misprints in the signs. These errors are corrected and the complete formulas for symmetrically located rectangles are given in Scientific Paper [11] No. 47.

As special cases of these formulas or by direct integration other formulas can be obtained for more special cases, such as lines and points. The formulas for a number of such special cases are given below in Appendix A.

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[7] B. O. Peirce, A Short Table of Integrals, No. 523, p. 65.
[8] B. S. Bull., **8**; 1911.
[9] B. S. Bull., **14**; 1918; B. S. Sci. Paper No. 320.
[10] Absolute Measurements, **2**, pt. 1, pp. 288–306.
[11] B. S. Bull., **3**, p. 6; 1907.

As an example of the procedure outlined above we may consider a shunt of the type [12] shown in Figure 2. Here the circuit between the current terminals C_1 and C_2 consists of the bars AD and DG of resistance material, joined at D. The potential circuit between P_1 and P_2 is connected to the current circuit at B and F, and over the length l_1 the leads BC and FE are held parallel to the bars opposite their center line. The various dimensions are indicated on the cross section XX'. From E and C the leads are brought off at right angles to the axis and are kept close together from there to the potential terminals.

The total inductance is, of course, the same as the mutual inductance between the total potential and current circuits, and this obviously consists of two parts contributed by the sections of length l_1 and l_2, respectively. Indicating directions and numbering the conductors in accordance with the rules given above shows that for the section

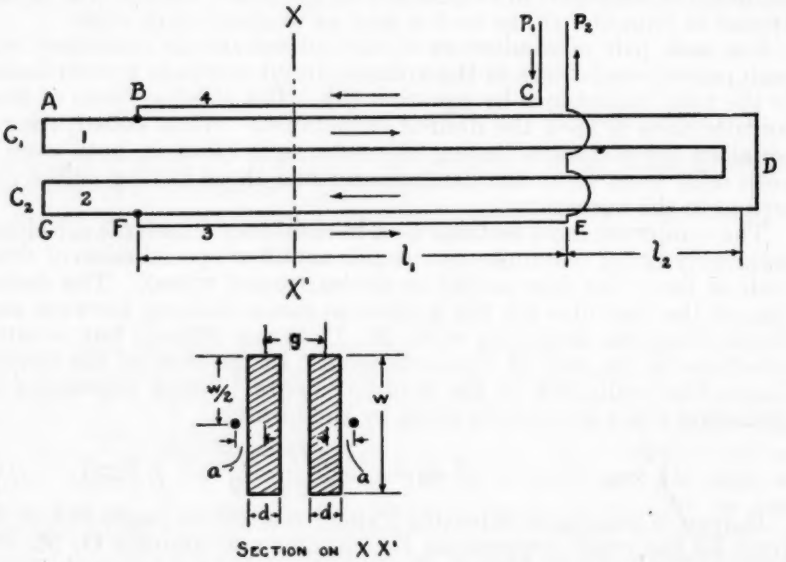

FIGURE 2.—*Flat strip shunt with compensating potential leads*

of length l_1 there is the one pair of current conductors 1 and 2, as well as the two pairs of potential conductors 1 and 2 and 3 and 4; while for the section of length l_2 there is the one pair of current conductors 1 and 2, but only one pair of potential conductors 1 and 2. We therefore have for the total inductance by equation (9)

$$L=2l_1\left[\log_e\frac{D_{12}\cdot D_{21}}{D_{11}\cdot D_{22}}+\log_e\frac{D_{14}\cdot D_{23}}{D_{13}\cdot D_{24}}\right]+2l_2\left[\log_e\frac{D_{12}\cdot D_{21}}{D_{11}\cdot D_{22}}\right] \quad (13)$$

Now, $D_{12}=D_{21}$ and also if the bars are of the same size and the potential leads are symmetrically placed $D_{11}=D_{22}$, $D_{14}=D_{23}$, $D_{13}=D_{24}$, hence,

$$L=4l_1\left[\log\frac{D_{12}}{D_{11}}+\log\frac{D_{14}}{D_{13}}\right]+4l_2\log\frac{D_{12}}{D_{11}} \quad (14)$$

[12] This type of construction is used in certain apparatus for current-transformer testing made by the Leeds & Northrup Co.

Inserting the values of the various geometric mean distances as given in the appendix yields, in case the thickness and spacings are small compared to the width of the bars,

$$L=4l_1\left[\frac{\pi\left(g-\frac{1}{3}d\right)}{w}-\frac{\pi(g)}{w}\right]+4l_2\left[\frac{\pi\left(g-\frac{1}{3}d\right)}{w}\right]$$

or

$$L=\frac{4\pi}{w}\left[-\frac{1}{3}dl_1+\left(g-\frac{1}{3}d\right)l_2\right] \tag{15}$$

This example brings out the fact that a fairly simple arrangement of the potential leads may introduce a compensating effect on the inductance of a shunt which may be of considerable utility. If the construction used in the section of length l_2 were used for the entire shunt, it would show a positive inductance of $+\frac{4\pi}{w}\left(g-\frac{1}{3}d\right)l$ millimicrohenries. If, on the other hand, the construction used in the section of length l_1 was extended over the entire length, the inductance would be negative and have the value $-\frac{4\pi dl}{3w}$. Hence, by choosing the lengths in the ratio given by

$$\frac{l_1}{l_2}=\frac{g-\frac{1}{3}d}{\frac{1}{3}d} \tag{16}$$

a shunt can be constructed having zero effective inductance.

III. END EFFECTS

The resistors actually used in the measurement of heavy currents are far from being infinite in length, and it might be thought that the formulas discussed in the foregoing paragraphs would have little applicability. That this is not the case, can be seen from a study of Figure 3. Here *A B C D E F G H* is the current circuit of a shunt of finite length, the potential circuit being *J K D C L M*. Let us superpose on this system the additional conductors shown in the dotted lines, which coincide with the actual conductors along *EF* and *BG*, and which extend to an indefinitely great distance at *NP* and *RS*. When currents are flowing in these additional conductors, as shown by the dotted arrows, the 4-terminal inductance of the shunt will be exactly that corresponding to a length l of a system of infinitely long straight conductors and may be designated by L_∞. If the inductance of the actual 4-terminal resistor is L_l, then the difference L_l-L_∞ may be called the "end effect."

It is evident that this difference is the result of and is equal to the mutual inductance between the potential circuit *J K D C L M* and the superposed loops *N E F P* and *R B G S*. In most cases the transverse dimensions a and g are small compared with the working length l of the shunt and this mutual inductance is very small. This is particularly true if the current circuit is made longer than the distance between potential taps as shown at k and m. Measurements on shunts made of flat sheet material have shown end effects

less than 10 per cent of the self-inductance of the shunt in cases where both the width and the spacing of the strips were as great as 80 per cent of the length of the shunt. It is therefore evident that the formulas derived on the basis of infinitely long conductors may be satisfactory guides even in cases of short, thick shunts.

The two forms of shunt most frequently chosen for use as computable standards of inductance are either a pair of flat strips close together or a pair of concentric tubes. Experiments[13] on shunts of

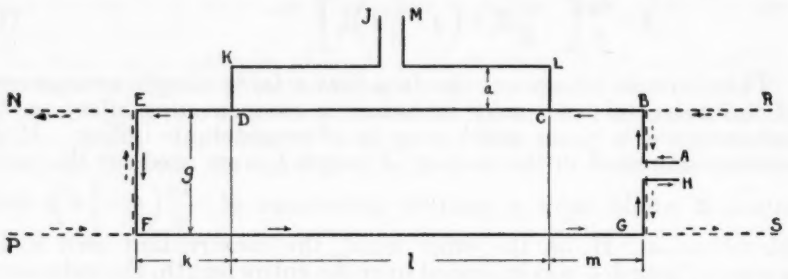

FIGURE 3.—*Illustration of end-effects in four-terminal resistance standard*

the former type have indicated that the end effect is quite negligible when the strips were close together and of reasonable length.

The end effect in shunts in which the current flows longitudinally in a pair of coaxial tubes of circular section joined at the ends by annular conductors is rigorously zero, provided that the magnetic field is not affected by the current flow in the current terminal blocks, and that the current is distributed uniformly around the axis. It will be seen that such a shunt is equivalent to the toroid formed by rotating a rectangle about an external axis which is parallel to the long sides of the rectangle.

It has been shown by Maxwell and others[14] that such a toroidal circuit produces no magnetic field whatever at external points. Furthermore, the end extensions required to make the transition from the actual shunt to the ideal pair of infinitely long conductors also constitute similar toroids, and hence can produce no magnetic field and no electromotive force in the potential circuit.

IV. ATTACHMENT OF POTENTIAL LEADS

In the case of shunts which are not intended to serve as computable standards of inductance, it is often convenient to attach the potential leads to small ears partially cut from the sheet manganin by a U-shaped slot as indicated in Figure 4 at *A* and *B*. This form of construction has long[15] been used in resistance standards and makes it possible either to increase or decrease the effective 4-terminal resistance of the standard over a moderate range by filing at the ends of the U at *A* or at *B*, respectively.

It will be seen, however, that this construction materially disturbs the streamlines of current over an area somewhat larger than the

[13] B. S. Bull., **13**, p. 396, 1916; B. S. Sci. Paper No. 281.
[14] Maxwell, Electricity and Magnetism, 3d ed., **2**, p. 313, sec. 681; Webster, Electricity and Magnetism, p. 451; 1897.
[15] W. Clark Fisher, The Potentiometer and Its Adjuncts, p. 72; 1902.

entire ear, and thus in effect superposes on the normal magnetic field of the shunt a small local bundle of magnetic flux. This flux is linked with the potential circuit at one end of the shunt (*A*, fig. 4) and will, therefore, contribute a certain amount to the effective inductance of the standard. Approximate calculation and some measurements on an experimental shunt indicate that this effect, though small, may introduce errors amounting to more than 1 millimicrohenry. Consequently, this form of attachment should be avoided in shunts which are to be used as computable inductance standards.

An alternative arrangement which permits of adjustment of resistance in either direction over a sufficient range without producing an appreciable effect on the inductance is shown by the potential connections on the lower side of the tubular shunt in Figure 4. Lead *EL* is soldered to the shunt at *E*. Leads *F* and *G* are similarly attached at such a distance from *E* that the resistance between *E* and *G* is greater and that between *E* and *F* is less than the nominal resistance of the shunt. The leads from *F* and *G* are joined by a resistor *HK*, and the binding post *M* is connected to an intermediate tap point *J*. Adjustment of the 4-terminal resistance is then obtained by unsolder-

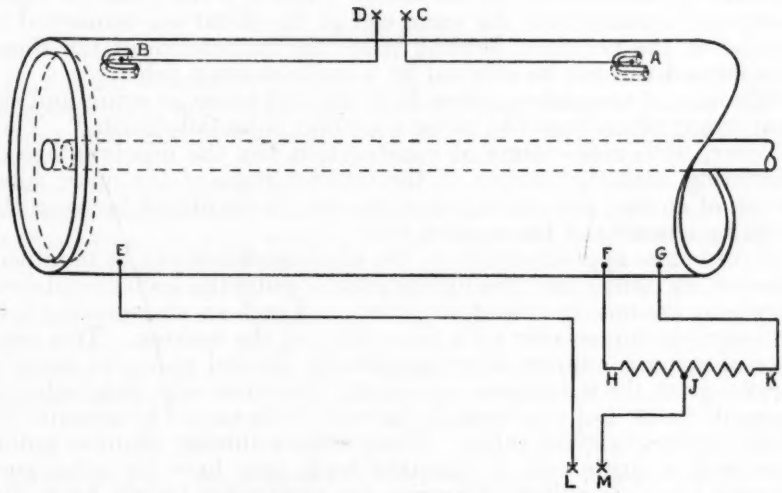

FIGURE 4.—*Alternative methods of connecting potential leads so as to admit of resistance adjustment*

ing tap *J* and moving it to the desired position without tampering with the main current-carrying portion of the shunt. Of course, a certain current flows through the leads and the resistor *HK*, but this is very small, since *HK* may be chosen to have a resistance several thousand times that of the part of the main conductor lying between *F* and *G*. The possible range of adjustment is, of course, approximately $\frac{FG}{EG}$, and it can be shown that the effect of this potential circuit on the time constant of the shunt as a whole is always less than the product of this range of adjustment and the time constant of the circuit *F H K G*. Since this latter circuit is of fairly high resistance, it is easy to make the product of these two small factors negligibly small.

The location of the potential leads in their course from the point where they are attached to the current circuit to the potential binding posts is usually fixed by the requirement that the 4-terminal inductance be as definite and as small as possible. In certain cases where the current-carrying parts are symmetrical there is still a certain latitude in the placing of the potential leads. This is especially true in the case the current circuit is formed of coaxial cylinders, for such a circuit produces no magnetic field at points outside or inside of both cylinders. The inductance is therefore the same for any location of the potential leads, provided they do not pass through the region between the tubes. However, if only a single pair of leads is attached to such a shunt, and if, for instance, only the outer tube is used as a resistor, the complete potential circuit may constitute a loop of considerable area, and hence be very susceptible to stray magnetic fields. If a second pair of potential leads is attached to the outer tube at points diametrically opposite to the points of attachment of the first pair, and if the two leads of each pair are tied down close to the elements of the cylinder joining their points of attachment, then the emf induced in one potential circuit by a uniform stray field is equal and opposite to that induced in the other. Hence, if the leads (of equal resistance) coming from the same end of the shunt are connected in parallel at the potential binding posts the inductance of the shunt thus formed will not be affected by a uniform stray field.

Of course, a nonuniform stray field will still cause an error, and the ideal arrangement would be to use a tubular potential sheath.[16] This, however, with most forms of construction has the disadvantage of interfering with the cooling of the outer surface of the outer tube, unless, of course, the cooling medium can be circulated between the potential sheath and the resistor tube.

A very close approximation to the ideal condition can be obtained, however, by using only three or four pairs of potential leads placed symmetrically around the axis of the shunt, and such an arrangement does not interfere appreciably with the cooling of the resistor. This principle of using a number of symmetrically located potential leads in parallel gives the inductance an independence not only from external magnetic fields, but also from the internal fields caused by eccentricity of the current-carrying tubes. Thus, while a tubular shunt of radius c cm with a single pair of potential leads may have its inductance changed by 2 q/c millimicrohenries per centimeter length by a displacement of q cm between the axes, the use of four pairs of leads spaced 90° apart reduces this change to only 3 q^4/c^4 millimicrohenries per centimeter. Furthermore, measurements made on the apparent inductance of the shunt, when the different pairs of leads are used separately, give a basis for estimating the amount and direction of the effective eccentricity in the current distribution. If L_1, L_2, L_3, and L_4 are the observed inductances, then

$$q=\frac{\sqrt{(L_1-L_3)^2+(L_2-L_4)^2}}{4\,c} \tag{17}$$

and

$$\tan\,\alpha_1=(L_2-L_4)/(L_1-L_3)$$

[16] Paterson and Rayner, Inst. Elec. Eng. J., **42**, p. 455; 1909.

where α_1 is the angle between the line joining the axes of the two tubes and the line joining the axis of the outer tube to potential lead 1, both lines being taken as lying in a plane normal to the axes.

It is, of course, not possible to locate the points of attachment of all the potential leads, which are grouped near one end of the shunt, on exactly the same equipotential surface. For this reason it is well to insert a resistance of a few tenths of an ohm in each potential lead, so that the currents circulating in the leads will be small. If the impedances in the various pairs of potential leads are equal, each pair will have equal weight in determining the potentials of the binding posts and the effective impedance of the shunt will be equal to the mean of the values observed by using the pairs separately. Any variation in the distribution of current over the current terminals of the shunt usually will affect differently the voltage drop between different potential leads, so that the mean value obtained by using a number of pairs of leads in multiple will be less affected by such sources of error. The resistance of the potential circuit is, of course, somewhat increased if these equalizing resistances are inserted, but for most purposes this resistance is not objectionable.

V. SKIN EFFECT

In normal laboratory practice, standards of resistance are intercompared and maintained by bridge measurements using direct current, and such methods are used to determine the resistance even of the standards which are to be used with alternating currents. It is therefore of importance in the design or use of alternating-current resistance standards to make sure that the effective resistance of the standard to alternating current of the frequency used does not differ from its direct-current resistance by a significant amount.

It can be shown by general dimensional reasoning that if the alternating-current resistance per unit length of a conductor depends only on the size and shape of the conductor, its resistivity ρ, its permeability μ and the frequency f of the current, then the ratio of the alternating-current to the direct-current resistance must be a function of the dimensionless parameter $\frac{\mu f D^2}{\rho}$, where D is some linear dimension of the cross section of the conductor. This principle has been stated more definitely by Dwight [17] for the case of nonmagnetic material, as follows: "In any conductor or combination of conductors or in any return circuit, of a certain proportionate shape, a given value of $\frac{f}{R}$ corresponds to a certain value of $\frac{R'}{R}$." Here R' and R are the alternating-current and direct-current resistances per unit length, respectively. A more mathematical proof of this principle has been given by Slepian [18] in his discussion of Dwight's paper.

Since manganin has a resistivity about twenty-five times that of copper, the skin effect in a structure of this material is the same as that in a similar structure of copper either having its transverse dimensions one-fifth as great or at one twenty-fifth the frequency and with the same dimensions. It is evident from this that the skin

[17] H. B. Dwight, Trans. A. I. E. E., **37**, pt. 2, p. 1398; 1918.
[18] J. Slepian, Trans. A. I. E. E., **37**, pt. 2, p. 1407; 1918.

effect in a resistance standard will usually be relatively small; but, on the other hand, the accuracy needed in resistance standards is much greater than that considered in engineering work with copper conductors.

If the shunt has the form of a return circuit formed of two thin, wide conducting strips in parallel planes placed close together, the lines of magnetic force over the central portion of the structure are parallel to the width of the strip. The intensity of the field at the center is 4π times the current per unit width of strip, and the intensity of the field at the outer surface of either strip and at points outside is zero. The emf induced by the alternation of a field having this distribution tends to make the current crowd toward the inner surfaces of each strip. The magnitude of this effect has been calculated by various writers for this case and for the analogous case of flux distribution in an iron lamination.

For low frequencies the ratio of the alternating-current resistance R' to the direct-current resistance R can be expresssed as a power series in terms of the dimensionless parameter $m\,d$; where d is the thickness of the strip in cm and m is defined by

$$m^2=\frac{8\,\pi^2 f}{\rho}=\frac{4\,\pi\,\omega}{\rho} \tag{19}$$

where ρ is the resistivity in cgs units (10^{-9} ohm-cm) and f is the frequency in cycles per second. For copper at 60 cycles $m=1.65$ while for manganin at this frequency $m=0.33$.

For the case of two strips close together and so wide that the effect of their edges is negligible the calculations [19] give for the skin-effect ratio

$$\frac{R'}{R}=1+\frac{m^4\,d^4}{45}-\frac{m^8\,d^8}{4{,}725} \tag{20}$$

If, however, the strips are separated so far that they exert no appreciable electromagnetic effect on each other, there is a tendency for the current to crowd toward the edges of the strips as well as to the flat surfaces. This additional effect is much larger than that given by equation (20). This case has also been analyzed mathematically by Dwight,[20] who obtains for low frequencies the equation

$$\frac{R'}{R}=1+0.0087432p^4-0.000384p^8+0.0000189p^{12} \tag{21}$$

where $p^2=\frac{m^2\,dw}{\pi}$, w being the width of the strip.

When the strips are separated by a moderate distance, the mathematical calculations, while still, perhaps, possible by Dwight's method, would certainly be very laborious. This problem has been attacked experimentally by Kennelly, Laws, and Pierce,[21] who have made an extensive series of measurements on the skin effect in conductors of a variety of shapes. Their data on copper strips $\frac{1}{16}$ inch thick and $\frac{1}{2}$,

[19] H. B. Dwight, Elec. Jn., **13**, p. 157; 1916.
[20] H. B. Dwight, Trans. A. I. E. E., **37**, pt. 2, p. 1397; 1918.
[21] Experimental researches on skin effect in conductors, Kennelly, A. E., Laws, F. A., and Pierce, P. H., Trans. A. I. E. E., **34**, pt. 2, p. 1953; 1916.

1, and 1½ inches wide at frequencies up to 5,000 cycles indicate that equation (21) correctly represents the result of the tendency of the current to concentrate in the edges of the strip, but that even with conductors twenty-four times as wide as they are thick and at a spacing of only one-third of their thickness this edge effect is still so great at 4,000 cycles as to give a skin effect ratio of 1.4 instead of the value 1.04 computed by equation (20).

It is difficult to extrapolate the results of Kennelly, Laws, and Pierce to smaller values of the parameter m. Consequently, a number of measurements were made at the Bureau of Standards on the resistance of an experimental manganin [22] shunt at frequencies up to 1,400 cycles per second, in order to obtain an indication of the magnitude of the resistance changes to be expected in this range.

The experimental shunt consisted of two strips 10 cm wide by 0.2 cm thick. These were joined to each other at one end and were

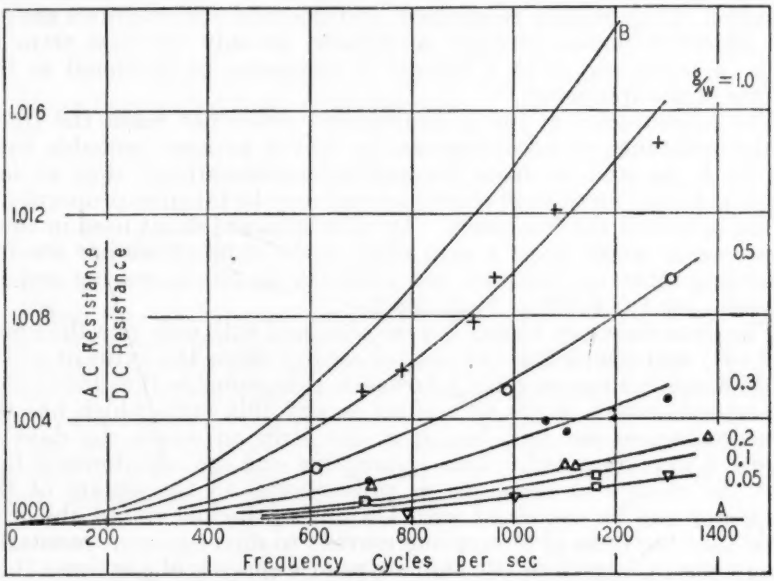

FIGURE 5.—*Ratio of a. c. resistance to d. c. resistance as a function of frequency, as observed on manganin strips 2 mm thick and 10 cm wide at various spacings*

Curve *OB* shows the theoretical value for infinite spacing and curve *OA* for zero spacing. Intermediate curves correspond to the values of the ratio of spacing g to width w marked opposite each curve.

provided with current terminals at the other. The total length from the current binding posts to the closed end was about 100 cm, and the potential taps were located one on each strip 70 cm from the closed end. The spacing could be adjusted from a maximum value of 10 cm to a minimum of 0.5 cm.

[22] Unfortunately, this shunt (which had been designed for another purpose) included at its closed end a section of sheet copper 15 cm long, 10 cm wide, and 0.022 cm thick. This piece of copper was sufficiently flexible to permit of ready adjustment of the spacing between the manganin strips, but it contributed about 0.00012 ohm to the total resistance of the shunt, which was about 0.00247 ohm for direct currents. The measuring current was maintained quite definitely at 80 amperes in all the measurements, but variations in the temperature of the copper considerably affected the precision of the results, and may have caused the skin effect to be slightly greater than that which would occur in a similar structure made entirely of manganin.

The resistance of this shunt was compared with that of a tubular shunt also of manganin. This latter shunt had a resistance of 0.0009285 ohm, the diameter of the tube being 5.1 cm and the thickness 0.15 cm. It had, of course, no edge effect, and its change in resistance with frequency as computed from the formulas given below was entirely negligible. The results are plotted in Figure 5, the ordinates being the ratio of alternating current to direct-current resistance while the abscissas are frequency. The curves OA and OB, of which OA practically coincides with the axis of frequency, are computed from equations (20) and (21), respectively. The observed points are indicated by crosses, and it will be seen that the increase in resistance with frequency at each spacing follows the same general trend as the curve OB corresponding to an infinite spacing, though to a less extent. Thus, the change in resistance at 10 cm spacing is about 60 per cent, while that for the ½ cm spacing is 6 per cent of the change computed for infinite spacing. For the frequencies used equation (21) is rapidly convergent and the solid curves drawn among the observed points actually correspond to only the first term of such a series and show a change of resistance proportional to the square of the frequency.

The inaccuracies in the measurements somewhat mask the trend of the resistance at lower frequencies, but it appears probable from Figure 5, as well as from theoretical considerations, that at low frequencies the increase in resistance still may be taken as proportional to the square of the frequency. On this basis the shunt used in these experiments would have a skin effect ratio at 60 cycles per second, exceeding unity by 350 parts per 1,000,000 at 10 cm spacing and by 50 parts per 1,000,000 at 1 cm spacing.

The data shown in Figure 5 were obtained with only one thickness (0.2 cm) and one width (10 cm) of strip. Since the ratio of width to thickness is so great (50:1), however, it is probable that the results are representative of the skin effect in any thin strip which has the same resistance per unit length as the strip on which the data of Figure 5 were obtained. This assumption and the experimental fact that the change in resistance is proportional to the square of the frequency can be combined with Dwight's principle stated above to show that the ratio of alternating current to direct-current resistance of any circuit formed of two thin strips at a spacing of g/w times their width is given for any frequency f, thickness d, and resistivity ρ by the equation

$$\frac{R'}{R}=1+\frac{f^2d^2w^2}{\rho^2}\cdot\frac{\rho_0^2}{f_0^2d_0^2w_0^2}\,(F_0(g/w)-1) \qquad (22)$$

where $F_0(g/w)$ is the ratio of alternating-current to direct-current resistance given in Figure 5 for the same ratio g/w of spacing to width and for $d_0=0.2$ cm, $w_0=10$ cm, $\rho_0=38{,}600$ c. g. s. units, and for the value of f_0 indicated by the abscissa.

Equation (22) is, of course, applicable only at low frequencies where the parameter p (equation (21)) is less than 0.5 and for strips so thin that the concentration of current at the edges is the predominating effect (that is, perhaps $d/w \lessapprox 0.2$).

As an example of the use of equation (22) consider the skin effect at 60 cycles for a circuit consisting of two copper strips 25 cm wide

and 0.5 cm thick, spaced 10 cm center to center. Taking $\rho = 1{,}750$ c. g. s. units, the factor $\frac{f^2 d^2 w^2}{\rho^2}$ is 0.184. The ratio of spacing to width is $g/w = 0.4$ and from Figure 5 for $f_0 = 1{,}200$ cycles we get by interpolating between the curves, $F_0\ (g/w) = 1.0063$, while the factor $\frac{\rho_0^2}{f_0^2 d_0^2 w_0^2}$ is 258. Hence, the skin-effect ratio for the copper strap is $1 + 0.184 \times 258 \times 0.0063 = 1.030$.

The skin effect in shunts of the tubular type can be computed mathematically. The case of a circular wire or tube with the return circuit at a great distance has been treated by a number of writers.[23] For low frequencies the ratio of alternating-current to direct-current resistance can be expressed by the first two terms of a power series, as follows:

For a solid wire of radius a

$$R'/R = 1 + \frac{m^4 a^4}{192} \tag{23}$$

For a thin-walled tube of thickness d

$$R'/R = 1 + \frac{m^4 d^4}{45} \tag{24}$$

where as before $m^2 = \frac{8\pi^2 f}{\rho}$

When the current-carrying circuit consists of two concentric tubes, the situation is more complicated. Russell [24] has published a very thorough study of the effective resistance and inductance of a concentric main, developing formulas both for low and for high frequencies. His equations can be still further simplified if we limit ourselves to low frequencies and to cases where the walls of the tubes are thin in comparison with their diameter. For this case Russell's equation (101) reduces to

$$R' = \frac{\rho}{\pi a^2}\left(1 + \frac{m^4 a^4}{192}\right) + \frac{\rho}{\pi(c^2 - b^2)}\left(1 + \frac{m^4 d^4}{45}\right) \tag{25}$$

where R' is the effective alternating-current resistance per unit length of the concentric main which is formed of a tube having outer and inner radii c and b, respectively, and a coaxial return conductor in the form of a rod of radius a. As before $d = c - b$. When the inner conductor is also a thin-walled tube of thickness d_1, Russell's equations (113) and (114) give

$$R' = \frac{\rho}{\pi(c^2 - b^2)}\left(1 + \frac{m^4 d^4}{45}\right) + \frac{\rho}{2\pi\left(a d_1 - \frac{d_1^2}{2}\right)}\left(1 + \frac{m^4 d_1^4}{45}\right) \tag{26}$$

[23] See bibliography in paper by Kennelly, Laws, and Pierce, referred to in footnote 21.

[24] A. Russell, The Effective Resistance and Inductance of a Concentric Main and Methods of Computing the Ber and Bei and Allied Functions, Phil. Mag., 6th series, **17**, p. 524; 1909.

Considerable caution must be exercised in passing from these cases to those in which the potential leads span a part of only the outer or of the inner conductor and are located entirely outside the outer tube or inside the inner tube.

The difficulty in separating the potential drops in the two conductors arises from the fact that the outer tube, if it has a finite thickness, receives power by transformer action from the inner conductor. Hence, its mere presence in the magnetic field of the inner conductor would increase the power drawn from the source even if the outer tube were not in metallic contact with the alternating-current circuit. The total resistance given by equation (25) or equation (26) must be considered as that quantity which, when multiplied by the square of the total current, gives the total power consumption. An integration of the quantity $i^2\rho dv$ over the cross section of the inner conductor, using for the current density i the value given in Russell's equation (65), shows that the power dissipated as heat in the inner conductor per unit length is given by

$$H_1 = I^2 \frac{\rho}{\pi a^2}\left(1+\frac{m^4a^4}{192}\right) \tag{27}$$

Hence, the heat developed in the outer conductor must be

$$H_2 = \frac{I^2\rho}{\pi(c^2-b^2)}\left(1+\frac{m^4d^4}{45}\right) \tag{28}$$

The potential drop in unit length of the outer conductor can be evaluated either from Russell's equation (78) by taking $i'\rho$ for $r=c$ and substituting the proper values for the constants A, B, C, D, and i_0, or by a direct solution of the differential equations in terms of Bessel functions to which Taylor's theorem can then be applied. The result by either method gives for the component of the voltage drop in phase with the current

$$E = \frac{\rho I}{\pi(c^2-b^2)}\left(1-\frac{7}{360}\,m^4d^4\right) \tag{29}$$

This indicates that such a shunt will actually have less effective resistance to alternating than to direct currents, but this is quite consistent with the fact that the current tends to crowd toward the inner surface of the outer tube.

Multiplying equation (29) by the current and subtracting the result from equation (28) gives as the power transferred from the inner to the outer conductor by transformer action

$$P = I^2 \frac{\rho}{\pi\,(c^2-b^2)}\,\frac{m^4d^4}{24} \tag{30}$$

Adding this to equation (27) and dividing by the square of the current gives for the resistance of the inner conductor as measured with potential leads brought out radially through holes in the outer tube

$$R_i = \frac{\rho}{\pi a^2}\left(1+\frac{m^4a^4}{192}\right)+\frac{\rho}{\pi\,(c^2-b^2)}\,\frac{m^4d^4}{24} \tag{31}$$

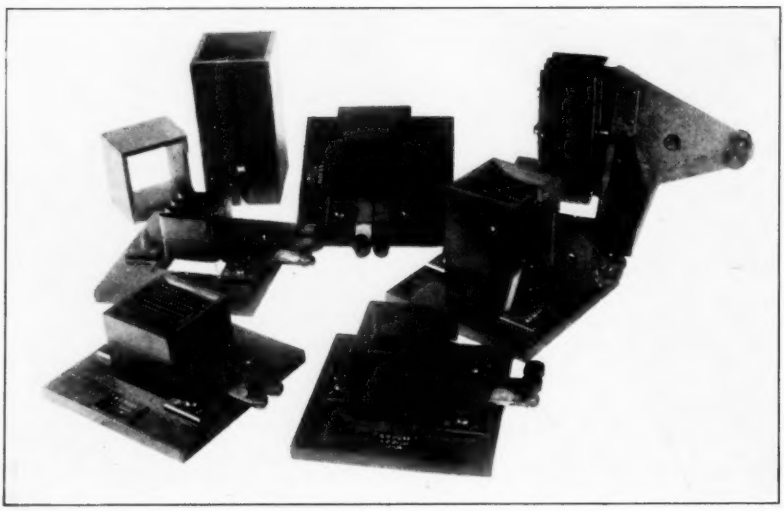

FIGURE 6.—*Group of air-cooled shunts ranging in resistance from 0.05 to 0.001 ohm and in current capacity from 10 to 500 amperes*

If, however, the potential leads are brought out through the hollow center of a tubular inner conductor we have

$$R_t = \frac{\rho}{2\pi\left(ad_1 - \frac{d_1^2}{2}\right)}\left(1 - \frac{7m^4 d_1^4}{360}\right) \tag{32}$$

where d_1 is the thickness of the inner conductor.

It is interesting to note that equation (28) indicates that for the case of two tubes of equal thickness and both so large as to have nearly the same radius the ratio of alternating-current to direct-current resistance approaches the same value as that given in equation (20) for infinitely wide strips.

VI. AIR-COOLED RESISTANCE STANDARDS

As examples of the application of the principles of design which have been discussed in the preceding sections we may consider the two groups of alternating-current resistance standards which were constructed at the Bureau of Standards for use in the current transformer testing. The first group of shunts, built in 1923 by F. M. Defandorf and R. D. Wyckoff, range in resistance from 0.05 to 0.001 ohm and are designed for a voltage drop of 0.5 volt. Figure 6 shows the general appearance of these shunts, and Figure 7 shows the arrangement of potential leads, etc., in a typical shunt of this group. Table 1 gives the essential dimensions and other data.

TABLE 1.—*Data on air-cooled shunts*

Resistance ohms	0.05	0.02	0.01	0.005	0.0025	0.001
Current rating amperes	10	25	50	100	200	500
Length cm	75	75	75	65	76	72
Width do	1.6	4.0	8.0	7.0	13.3	20.0
Thickness do	.056	.056	.056	.081	.10	.14
Watts per square centimeter at rated current	.021	.021	.021	.055	.050	.083
Phase angle at 60 cycles, observed minutes	+.4	+.3	+.1	−.3	−.4	−2.0

The cooling of these shunts is effected by placing them in an air stream which is supplied by a motor-driven blower. The air is led from the blower through a hole in the table top and passes up through a wooden channel 11 by 11 cm, inside of which the shunt proper is located. The air velocity at full speed of the blower is about 1,600 cm per second (36 miles per hour), and the heat dissipated is 0.017 watt per square centimeter per degree centigrade temperature rise. Consequently, the temperature rise of the 500 ampere shunt at full-rated current is only 5° C., and that of the other shunts is considerably less. The cooling was found to be roughly proportional to the square root of the air velocity. This method of cooling avoids the risk of corrosion of the shunt metal by contact with oil which has become acid and eliminates the spilling and leakage usually associated with oil-cooled apparatus. The noise made by the blower is slightly objectionable at the highest speeds required to cool the largest shunts. The cooling surface required to transfer larger amounts of power than the greatest here used (250 watts) makes the design of air-cooled alternating-current shunts for higher ratings rather difficult, and the oil-

cooled shunts described below have been developed for higher current ranges.

While the general principle of compensating the inductance of shunts by suitably locating the potential leads has long been recognized,[25] most of the designs embodying this principle have involved

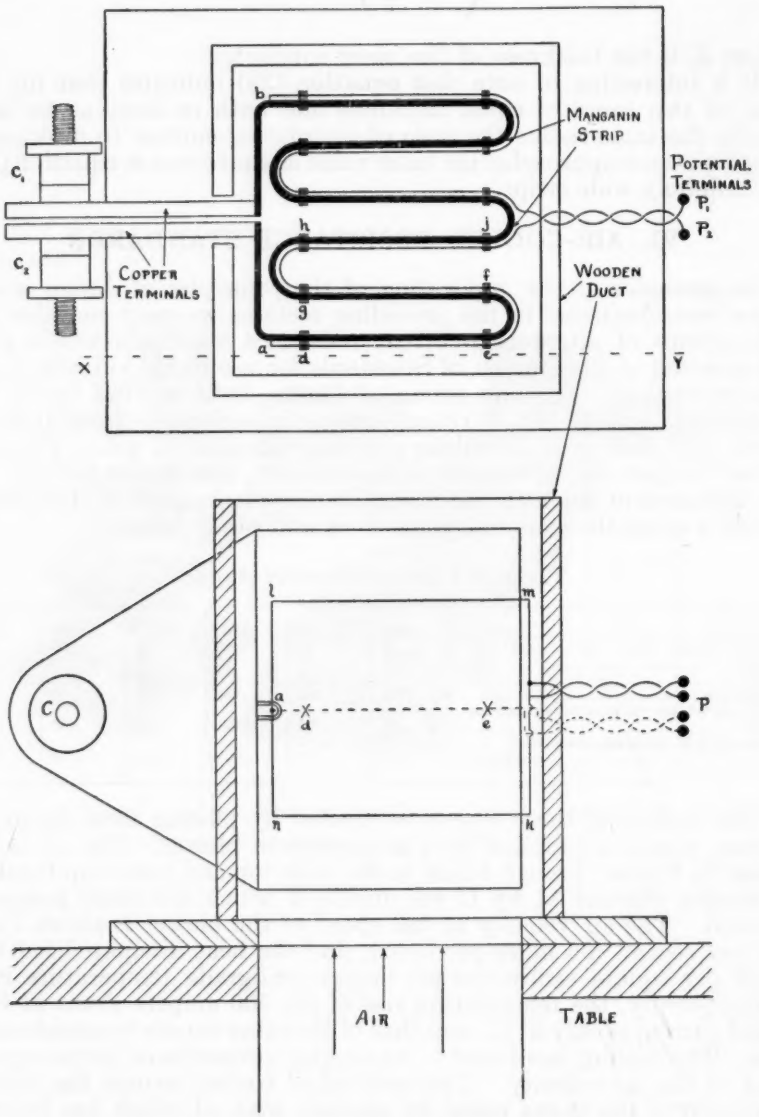

FIGURE 7.—*Plan and cross section of air-cooled shunt*

the use of a potential sheath which has covered one side of the working resistor, and thus has materially obstructed the available cooling surface. In this group of air-cooled shunts all possible cooling surface

[25] Campbell, Electrician (London), **61**, p. 1000; 1908.

is needed, and the current-carrying strips are therefore placed about 9 mm apart, so that both sides are exposed to the cooling air stream. The current circuit, therefore, produces a considerable magnetic field. The effect of this on the self-inductance of the shunt as a whole has been compensated by locating the potential leads as shown in Figure 7. The ends of the leads are soldered to U-shaped lugs at a and b, and each lead (of flattened No. 30 wire) is tied tightly against the manganin strip as at d, e, f, g, h, or l, m ---------- throughout its foldings to the center (j) of its length, where the two leads meet and run as a twisted pair to the potential binding posts p_1 p_2.

In the shunts of the lower four current ranges the potential leads are placed in the center of the width of the manganin strip, as indicated at de, Figure 7. This gives a sufficiently close compensation for inductance and skin effect, and renders the shunt practically immune to stray magnetic fields. In the case of the 200-ampere shunt the lead is placed as indicated at lm, Figure 7, and in the 500-

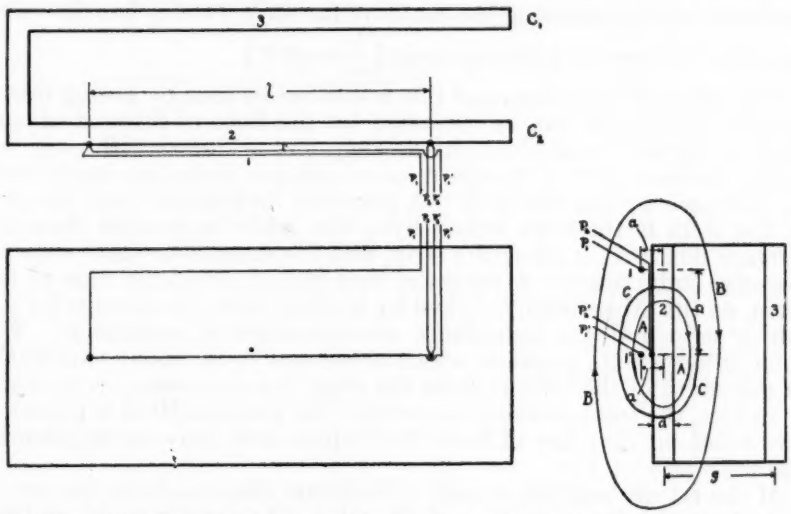

FIGURE 8.—*Schematic diagram of simple shunt with alternative potential leads*

ampere shunt two sets of potential leads connected in parallel are used as indicated at lm and nk, Figure 7. The placing of the leads down from the edge of the strip by a distance equal to two-tenths of the width of the strip has the effect as shown below of giving a more accurate compensation of inductance and skin effect, while the use of two leads in parallel restores the immunity to stray fields which is sacrificed by the unsymmetrical location of the single lead in the 200-ampere shunt.

The effect of the location of the potential leads in shunts of this type can be seen if we first consider the set of conductors shown in Figure 8. Assuming that the formula for long straight conductors is applicable, the 4-terminal inductance is given by

$$L = 2l\left[\log_e \frac{D_{12}\, D_{23}}{D_{13}\, D_{22}}\right]$$

$$= 2l[\log_e D_{12} - \log_e D_{22} + \log_e D_{23} - \log_e D_{13}] \qquad (33)$$

It will be seen that the first two terms are independent of the distance g to the return lead, and that if the return were at a great distance, so that $\log_e D_{13} = \log_e D_{23}$, the inductance would be given by

$$L = 2l[\log_e D_{12} - \log_e D_{22}] = 2lF_1 \tag{34}$$

If we limit ourselves for the present to the case of thin strips when a and d are zero, the equations I (c) and II (d) given in the appendix show that the factor in the brackets is given by

$$F_1 = \frac{1}{2} + n \log_e n + (1-n) \log_e (1-n) \tag{35}$$

where $n = \frac{1}{2} - \frac{b}{w}$. The quantity F_1 has the value $+0.5$ for $n=0$ or $n=1$ (that is, if the potential lead is run along either edge of the strip); it has a minimum value of -0.193 for $n=0.5$ (that is, if the potential lead is run along the center of the strip); and it has the value zero if $n=0.2$ or 0.8 approximately $\left(\frac{b}{w} = \pm 0.3\right)$.

The physical significance of this result can be seen by noting that a certain amount of flux as indicated by the lines of force A–A and C–C in Figure 8 cuts through the strip and is linked with only the center portion of it, although most of the flux links the entire strip as indicated by the line B–B. A potential lead placed near the axis of the strip is therefore linked by a flux which is greater than the average flux linking the entire strip, and the shunt as a whole shows a negative inductance. A potential lead placed along the edge of the strip, on the other hand, is linked by less flux than the average for the entire strip and the inductance compensation is incomplete. For some intermediate position, which works out to be about two-tenths of the width of the strip in from the edge, the compensation is exact.

In fact, the compensation is correct if the potential lead is placed at any point on that line of force C–C which cuts the central plane of the strip at $b = 0.3\ w$.

If the return lead 3 is at only a moderate distance from the rest of the shunt, the distances D_{13} and D_{23} will not be exactly equal, and the 4-terminal inductance will contain a contribution

$$2lF_2 = 2l[\log_e D_{23} - \log_e D_{13}] \tag{36}$$

which will depend on the spacing g between the strips. From the equations II(a) and I (a) given in the appendix it follows that for the case of thin strips

$$\begin{aligned} F_2 = {} & \frac{1}{2}x^2 \log_e x^2 + \frac{(1-x^2)}{2} \log_e (1+x^2) \\ & - \frac{n}{2} \log_e (n^2+x^2) - \frac{(1-n)}{2} \log_e \left\{(1-n)^2+x^2\right\} \\ & + x\left\{2 \cot^{-1} x - \cot^{-1} \frac{x}{1-n} - \cot^{-1} \frac{x}{n}\right\} - \frac{1}{2} \end{aligned} \tag{37}$$

where $x = \frac{g}{w}$. The function of x and n given by equation (37) is plotted in Figure 9 against x for several values of n, and in Figure 10 against

n for several values of x. These curves show that as the return strip 3 starting at a great distance is brought closer and closer to the outgoing strip 2 the term $2lF_2$ changes from zero in such a way as to tend to offset the inductance $2lF_1$ computed from the D_{12} and D_{22} terms. This tendency to compensation exists whether the original inductance is positive or negative, and in the limit when the strips are in coincidence so that g and x are zero, the compensation becomes perfect (that is, $F_2(o, n) = -F_1(n)$). This, of course, is to be ex-

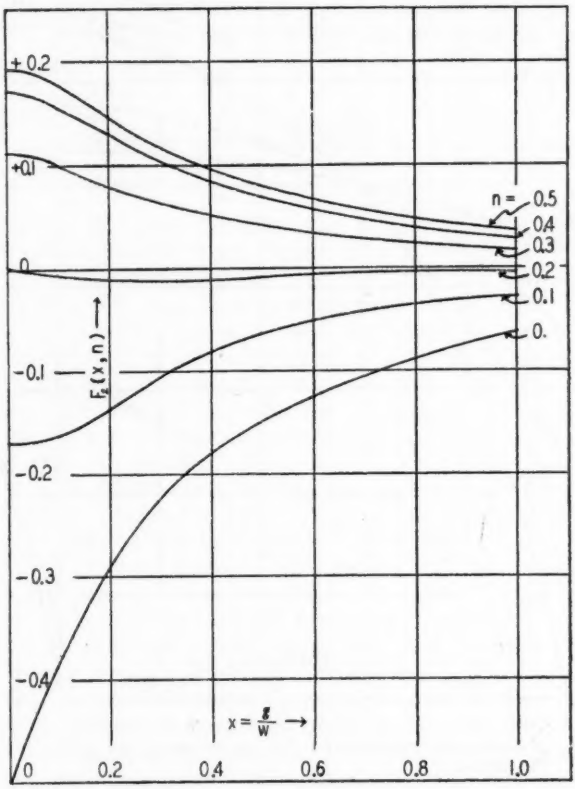

FIGURE 9.—$F_2(x, n) = \frac{1}{2}x^2 \log_e x^2 + \frac{(1-x^2)}{2}\log_e (1+x^2) - \frac{n}{2}\log_e (n^2+x^2) - \frac{(1-n)}{2}\log_e \left\{(1-n)^2+x^2\right\} + x\left\{2 \cot^{-1} x - \cot^{-1}) \frac{x}{1-n} - \cot^{-1}\frac{x}{n}\right\} - \frac{1}{2}$ *plotted as a function of x for the values of n marked on the curves*

pected, since when the strips coincide the outgoing and return currents completely neutralize each other, element by element.

Figure 9 also shows, however, that in case $n = 0.2$ or 0.8 the net effect of the return lead 3 is practically zero for all spacings. It is therefore evident that the location of the potential lead at either of these positions will cause complete compensation for the self-inductance of the current circuit and is especially desirable in designs, such as those described below, where the current-carrying parts form a zigzag path,

so that each potential lead is subject to the magnetic effect from a number of current strips.

In the actual construction of a shunt the current-carrying strips must, of course, have a finite thickness. If the thickness of each is d, the inductance will be less than that given by equations (35) and

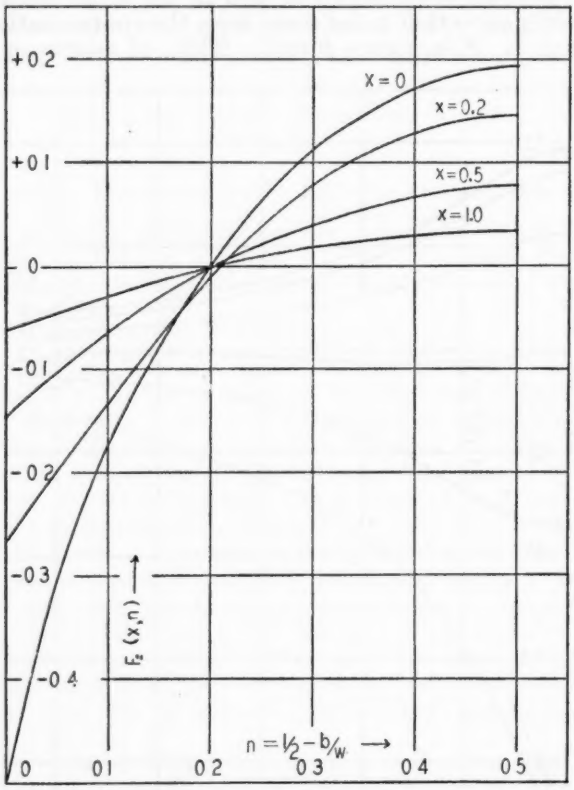

FIGURE 10.—*Graph of F_2 (x, n) given in equation (37) plotted as a function of n for the values of x marked on the curves*

(37). The correction resulting from the finite thickness is found from equations $I(c)$; $II(d)$, 2; $II(a)$ and $I(a)$ of the appendix to be

$$2lF_3 = 2l\left[-\frac{\pi}{3}\frac{d}{w}+\frac{d^2}{24\,w^2}\left\{\frac{25}{3}-\frac{1}{n(1-n)}-4\log_e\frac{d}{w}\right.\right.$$
$$\left.\left.-2\log_e\left(1+\frac{1}{x^2}\right)+\frac{n}{x^2+n^2}+\frac{(1-n)}{(1-n)^2+x^2}\right\}-\text{-----}\right] \qquad (38)$$

Inspection shows that for most values of $\frac{d}{w}$ and $\frac{g}{w}$ likely to occur the terms involving $\frac{d^2}{w^2}$ can be neglected unless n is nearly zero or unity.

Similarly the potential lead can not well be made to lie exactly in the medial plane of the strip, but is at a small distance a from this plane. In practice a will be slightly greater than $\frac{d}{2}$ because of the

insulation between lead and shunt. The effect of this spacing a is to add to the inductance a contribution

$$2lF_4 = 2l\left[\frac{a}{w}\left\{\pi \mp \tan^{-1}\frac{n}{x} \mp \tan^{-1}\frac{(1-n)}{x}\right\}\right.$$
$$\left. + \frac{a^2}{2w^2}\left\{\frac{(x^2+n-n^2)}{(x^2+n^2)\,(x^2+(1-n)^2)} - \frac{1}{n\,(1-n)}\right\} - \cdots\right] \qquad (39)$$

The upper signs apply when the potential lead and the return conductor lie on opposite sides of the strip, the lower signs when they are on the same side. Here, again, the terms in $\frac{a^2}{w^2}$ are negligible under all usual conditions. For close spacings (small values of g or x) the first-order term also becomes small while for large values of g or x it approaches the value $2\,\pi\,l\frac{a}{w}$.

In deducing equation (39) from the basic equation (33), the term $\log_e D_{12}$ has been taken from equation $I(c)$ in the appendix. The value of $\log_e D_{13}$ is obtained by putting $(g+a)$ in place of a in the general equation $I(a)$ and then expanding for a small.

In the arrangement actually used in the air-cooled shunts it will be seen from Figure 7 that each stretch of manganin strip and its part of the potential lead correspond to conductors 2 and 1, respectively, in Figure 8. In place of a single-return conductor as 3 in Figure 8 there is a succession of conductors which are spaced at consecutively greater and greater distances from conductor 2 and which carry currents which flow alternately in opposite directions. The inductance can, therefore, be estimated by adding to the result of equation (34) a succession of contributions computed by the use of equation (36) for the various other conductors. This procedure, of course, does not make proper allowance for the connections across the ends, but phase angles thus computed have been found in most cases to agree with experimentally observed values to within one minute at 60 cycles, after the corrections $2lF_3$ and $2lF_4$ have been applied.

It is evident from the foregoing paragraphs that this design offers a convenient means of obtaining a shunt of small and definite inductance. In the case of manganim shunts having a resistance of 0.01 ohm or more the correction terms $2lF_3$ and $2lF_4$ may be of the same order as the main terms $2lF_1$ and $2lF_2$, but the total phase angle is so small that a satisfactory design is obtained by running the potential lead at the center of the width of the shunt. With shunts of lower resistance made with wider and thicker strips the phase angle becomes of greater importance and it becomes more desirable to move the potential lead nearer to the edge of the strip to maintain sufficiently close compensation. Because of uncertainty in the distance a between potential lead and strip it is usually necessary to determine the exact value of inductance experimentally by comparison with a more readily computable standard.

Any theoretical estimate of the skin effect in shunts of this type is very difficult because of the fact that the potential lead is placed so close to the current-carrying parts that it is subject to a greater inductive action from some parts of the current than from others.

A general idea of the apparent resistance to be expected with such a construction can be seen from the following considerations. In

the case of a thin strip conductor with a return conductor at a moderate spacing the current density existing near the edges of the strip tends to lead in phase as compared with the total current, and also to be somewhat greater in magnitude than the average current density over the entire cross section. This is because the edges are linked by less than the average amount of magnetic flux. Conversely, the current density in the central portion of the strip lags in time phase behind the total current. Now, the total electromotive force induced in a potential lead, which is located, say, along the edge of such a strip, may be considered as the sum of contributions from elements of current flowing in all parts of the strip. Each contribution of emf is strictly in time quadrature with the element of current which produces it and is proportional in magnitude to the mutual inductance between the current element in question and the potential lead. This mutual inductance will be greatest, of course, in the case of those elements located nearest to the potential lead and, therefore, these elements of current (in this case those near one edge of the strip) will have more weight than the rest in determining the time phase of the total emf induced. The result is that the induced emf leads the quadrature position and has a component in phase with the current so that the total effective resistance of the 4-terminal conductor is greater than it would be if there were no inductive action. Conversely, a shunt having its potential lead placed near the center of the strip has an apparent negative skin effect. Furthermore, it would be expected that if the potential lead were placed in an intermediate location, so that the current elements near it had substantially the same phase as the total current, then the 4-terminal conductor would show only the normal skin effect corresponding to the actual increased power dissipation in the metal.

As a check upon the foregoing analysis, a series of measurements were made on the effective resistance, at frequencies of about 60, 600, and 1,000 cycles per second, of an experimental shunt which consisted of two parallel straight strips which formed the outgoing and return conductors. A number of pairs of potential leads were clamped against the outside of one of the strips at various distances from its axis. For convenience the points of contact between the potential leads and the strip were common to all the pairs of leads and were at two points on the center of the strip. Since the equipotential surfaces are necessarily planes perpendicular to the axis of the shunt the same results would have been obtained if the points of contact had been distributed along two such planes. The strip was of manganin 10 cm. wide and 0.2 cm. thick. The return circuit was formed of a similar straight strip which could be placed at various distances from the working strip but which carried no potential leads. The results are shown in Figure 11. Here the abscissas are the distance of the potential lead from the edge of the strip, expressed in terms of the width of the strip. The ordinates are the increase of the alternating-current over the direct-current resistance, divided by the direct-current resistance and by the square of the frequency, for the 4-terminal conductor formed by the strip and the potential lead placed as indicated by the abscissa. The several curves shown correspond to different spacings of the return conductor. The number on each curve is the ratio of the spacing between the strips to the width of the strip. Figure 11 is based mainly on data obtained with a fre-

quency of 1,000 cycles, but results at other frequencies showed the change in resistance to be roughly proportional to the square of the frequency.

It will be seen that the general trend of the curves is in accordance with what would be expected from the theoretical considerations previously discussed. The shunt when used with potential leads at or near the center of its width shows a very considerable decrease in resistance with increase of frequency, while if the potential lead lies

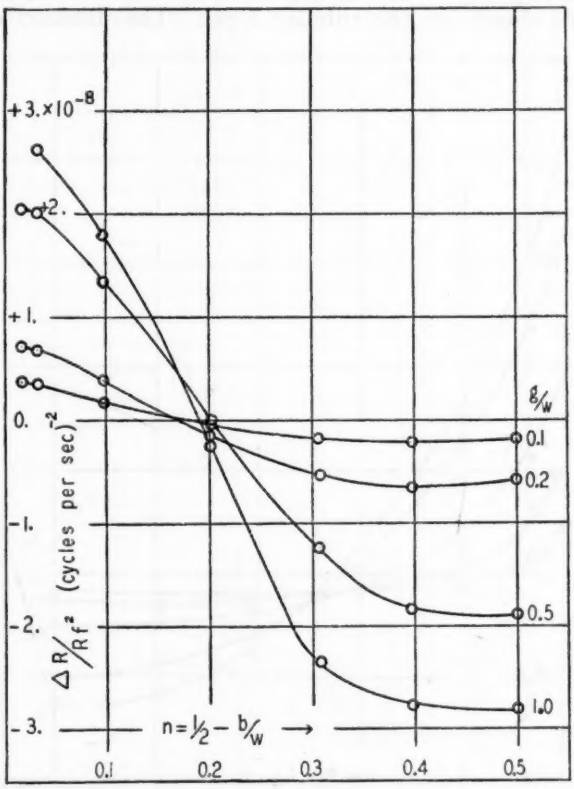

FIGURE 11.—*Observed relation between the four-terminal a. c. resistance of a flat-strip shunt and the location of the potential leads fastened tightly against the strip*

The abscissas are the distance measured parallel to the width of the strip from its edge to the potential lead, expressed in terms of the width of the strip. The ordinates are the increase in resistance from d. c. to a. c. divided by the d. c. resistance and by the square of the frequency. The number marked opposite each curve indicates the ratio of the spacing of the strips g to their width w.

near the edge the skin effect is positive. The position which gives zero net skin effect for the shunt is substantially the same as that corresponding to zero effective inductance and varies only slightly with the spacing to the return conductor.

Inductance measurements were also made on the experimental strip shunt as a check upon the theoretical equations. Figure 12 shows by the curves the net effective inductance per unit length of the experimental shunt as computed from equations (35) and (37) after correct-

ing for the thickness of the strip by equation (38) and for the location of the potential lead by (39). The plotted points show the values observed experimentally at 60 cycles. The agreement is quite satisfactory, and the small discrepancies can reasonably be attributed to uncertainty in the distance between the strip and the potential lead.

VII. OIL-COOLED RESISTANCE STANDARDS

The second group of alternating-current resistance standards consists of two shunts of the tubular type. The detailed design and

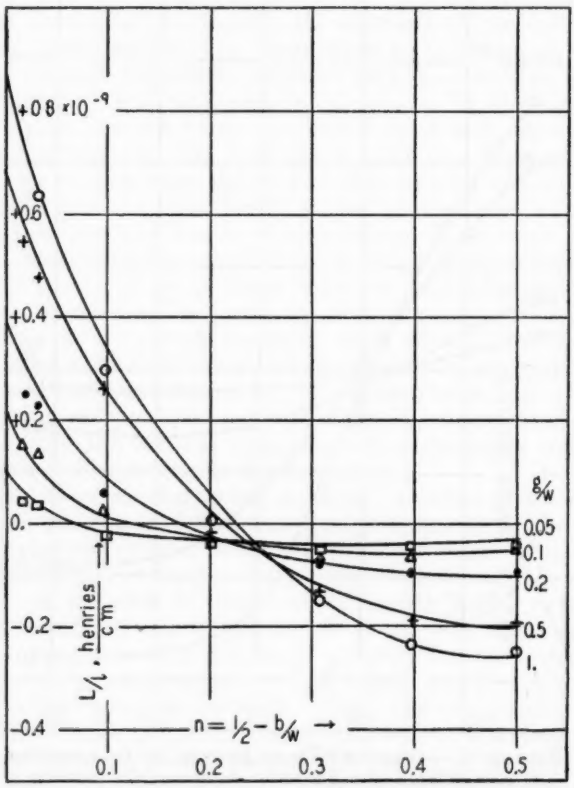

FIGURE 12.—*Four-terminal inductance per centimeter length of a flat strip shunt as a function of the distance of the potential lead from the edge of the strip expressed in terms of the width of the strip*

The number marked opposite each curve indicates the ratio of the spacing of the strips g to their width w.

adjustment of these shunts were worked out by R. D. Wyckoff and R. L. Smith. The mechanical construction was done by J. M. S. Kaufman. The shunts were completed early in 1929. One is rated at 1,000 amperes, 0.0005 ohm, and the other has a current rating of 2,500 amperes and has two sets of potential terminals corresponding to resistances of 0.00025 and 0.0002 ohm. The considerable amount of power dissipated as heat in these shunts makes the use of oil cooling desirable. The tubular construction was chosen as offering at once

convenient guiding surfaces for the cooling oil, freedom from any tendency to produce magnetic field at external points and the possibility of obtaining the inductance by computation without requiring comparison with any other shunt. Figures 13 and 14 show the general

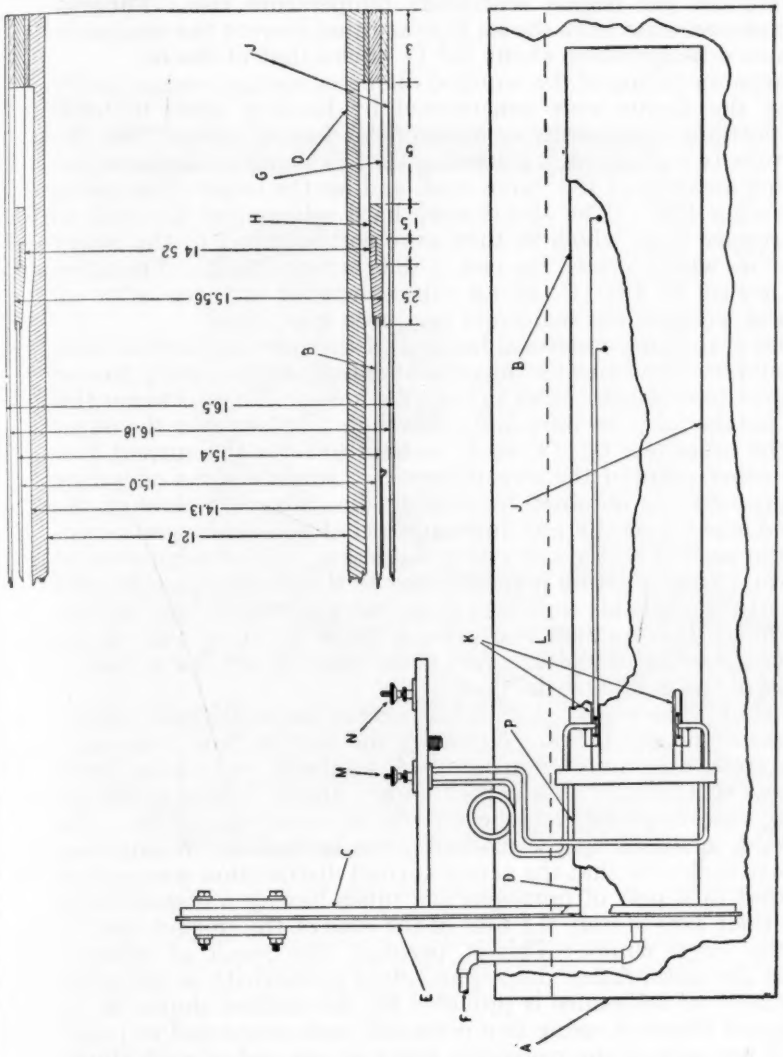

FIGURE 13.—*Diagrammatic view and partial longitudinal section of oil-cooled shunt*

A is oil tank; *B* is manganin tube connected to terminal slab *C* by the copper extension tube *F*; *D* is copper tube carrying the return current and connected to terminal slab *E*. Oil enters at *F* and passes through narrow ports in the copper tube into the annular space between the copper and manganin tubes. At the right end the oil passes through ports *G* in the copper extension *H* of the manganin tube *B* and returns through the annular space between the manganin tube *B* and the outer brass tube *J* to the exit ports *K* where it returns to the tank, filling it to the level *L*. *M* and *N* are the concentric potential binding posts for the 0.00025 and the 0.00020 ohm ranges.

appearance of these shunts, and Table 2 gives the essential data concerning them.

TABLE 2.—*Data on oil-cooled shunts*

Resistance	ohms	0.0005	0.00025	0.00020
Current rating	amperes	1,000	2,500	2,500
Length of manganin tube between potential leads	cm	35	64	51
Diameter	do	8.57	15.2	15.2
Thickness	do	.1	.2	.2
Watts per square centimeter at rated current		.27	.26	.26
Phase angle at 60 cycles, computed	minutes	−.7	−2.9	−2.9

Cooling is effected by a stream of oil (about 20 gallons per minute) which is circulated by a centrifugal pump through the annular spaces on each side of the manganin tubes. The linear velocity of the oil is about 65 cm per second, and the heat transfer is about 0.023 watt per square cm per degree centigrade temperature rise. Thermocouple measurements have shown that at rated current the manganin operates at a temperature about 11° C. above that of the oil.

As manganin tubing of the required diameter was not commercially available, the shunts were constructed by bending sheet material to form portions of a circular cylinder of the desired radius. For the smaller tube two pieces each extending the full length of the shunt and subtending an angle of 180° were used, and for the larger three pieces each covering 120°. The sheets were hard soldered at the ends to narrow copper rings which in turn were soft soldered to the heavy copper tubes which formed the rest of the current circuit. The tubes were annealed at 450° C. in an atmosphere of nitrogen after all mechanical work on the manganin had been completed.

Because of the unsymmetrical location of the current-terminal slabs there would be a tendency for the current density to be slightly greater in the upper part of both tubes than in the lower. To counteract this effect, a number of holes were drilled through the slabs near the upper side of the tubes (see fig. 14) so as to tend to force the current flow into the other parts of the circumference. A test for the adequacy of this procedure is obtained by sending direct current through the shunt and experimentally plotting some loci of points of equal potential on the surface of the tube near the slabs. These equipotential lines normally lie in planes perpendicular to the axis of the tube, and any departure from this condition is an index of nonuniform current distribution. This method also gives a fairly sensitive test of the quality of the soldered joints, a very small crack producing a marked distortion of the equipotential lines.

These shunts are provided with four sets of potential leads spaced 90° apart around the tubes. Normally the four leads of each equipotential group are connected in parallel to minimize errors from eccentricity and stray fields. As a preliminary check, however, the inductance was measured using each set of leads separately. The values when analyzed by the method given in Section IV (equation (17)) above indicated that the actual current distribution was equivalent to that in a pair of homogeneous tubes having a displacement between their axes of only 0.1 mm in the case of the smaller and 0.7 mm in the larger shunt. This is, perhaps, the result of inhomogeneity in the metal rather than of an actual eccentricity of the tubes.

Adjustment of resistance is provided by the method shown in the lower part of Figure 4, using two potential leads connected at points about 2.5 per cent of the resistance apart at one end of each shunt. All potential leads of the group connecting to the same equipotential surface are of the same length and resistance. Those running toward the closed end of the current circuit are of No. 18 manganin wire rolled flat and tied down tightly against the tube. Between the tube and the binding post one group of potential leads is formed by four slender copper or brass tubes, while the corresponding leads of the group from the other end of the shunt are drawn through these tubes, which thus function as conduits and also serve to keep the two leads

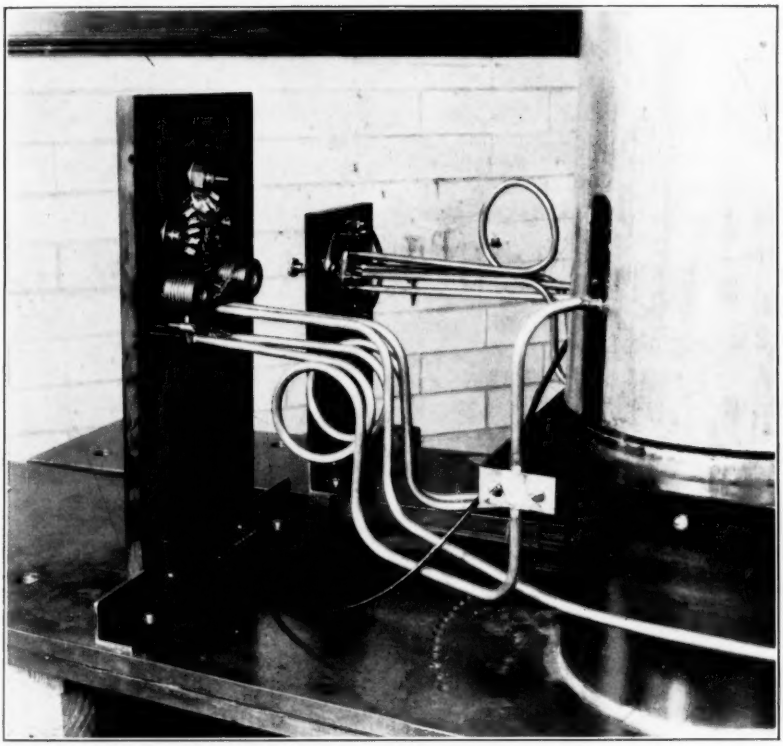

FIGURE 14.—*View of oil-cooled shunts removed from tank and placed with the axis of the current-carrying tubes vertical, to show the under side of the potential terminals, the resistors which serve for the exact adjustment of the resistances, and the tubular potential leads which serve as conduits for those other potential leads which are attached to the shunt along the same element*

of each set close together to avoid any loops which might link with stray fields. For the same reason the binding posts themselves are made concentric.

VIII. CONCLUSION

It will be seen from the foregoing sections that the design of a resistance standard for alternating current need not differ very greatly from that of a resistor for direct current. The prime considerations of resistance and cooling are the same for both. The requirements of a small and definite inductance can usually be met by proper attachment and location of the potential leads without greatly affecting the cooling. To avoid skin-effect errors somewhat more modification in design is required, but the symmetry of construction usually resorted to in alternating-current standards would probably lead to more uniform temperature distribution and better performance than the more conventional direct-current designs.

It is hoped that the descriptions given in Sections VI and VII of the resistors used at this bureau in current-transformer testing may be of assistance to other laboratory workers in preparing satisfactory designs. The choice of the tubular construction for the standards of greatest current-carrying capacity was dictated mainly by the consideration that the inductance would be computable from the dimensions. Now that these resistors are in existence others of different construction but of the same nominal resistance can be compared with them and, hence, there is less necessity for the construction of similar resistors in the future. It may be remarked, however, that the mechanical difficulty of constructing the necessary tubes from sheet material was found to be much less than had been anticipated, and that the advantages of freedom from stray fields and of nearly uniform temperature distribution throughout the working part of the shunt are not to be undervalued.

IX. NOTATION

a = coordinate of point (or potential lead) from center of rectangle (or strip) measured along shorter axis, or
a = outer radius of inner conductor of concentric main.
b = coordinate of point (or potential lead) from center of rectangle (or strip) measured along longer axis.
b = inner radius of outer conductor of concentric main.
c = outer radius of outer conductor of concentric main.
D = linear dimension.
D_{13}, D_{14}, D_{xy} = geometric mean distances between areas 1 and 3, 1 and 4, x and y, etc.
d = thickness of conducting strip.
d_{12}, d_{13} = distances between elements of conductors 1 and 2, 1 and 3, etc.
E = electromotive force.
F_1, F_2, F_3, F_4 = functions defined by equations (35), (37), (38), and (39), respectively.
f = frequency.
g = distance between centers of strips (or rectangles).

H_1, H_2 = heat developed in inner and outer conductors of concentric main.
I = current.
i = current density.
i_1, i_2 = current density in conductors 1, 2.
i' = current density in outer conductor of concentric main.
i_0 = current density at center of inner conductor of concentric main.
$j = \sqrt{-1}$.
k = constant of equation (12).
L = self inductance.
L_1, L_2 = inductance using potential leads 1, 2.
L_l = inductance of shunt of length l.
L_∞ = inductance of section of length l of a shunt of infinite length.
l, l_1, l_2 = axial lengths.
M = mutual inductance.
$M_{12, 34}$ = mutual inductance between circuit 12 and circuit 34.
$m = \sqrt{\frac{8\pi^2 f}{\rho}} = \sqrt{\frac{4\pi\omega}{\rho}}$.
P = power transferred by transformer action between conductors of concentric main.
$p = m\sqrt{\frac{dw}{\pi}}$.
q = displacement of axes.
R = direct-current resistance.
R' = alternating current resistance.
R_i = alternating-current resistance of inner conductor.
ΔR = change in resistance between alternating current and direct current.
r = radial distance.
S_1, S_2 = area of conductor 1, 2.
t = constant of equation 12.
v = volume.
w = width of strip.
y = variable of integration in equation 12.
$x = g/w$.
Z = impedance.
α_1 = angle between line joining axes of tubes and line joining axis of outer tube to potential lead 1.
μ = permeability.
ρ = resistivity.
φ_1, φ_2 = flux linkages due to current in conductors 1, 2.
ϕ = total flux linkages.
$\omega = 2\pi f$.

X. APPENDIX A.—FORMULAS FOR GEOMETRIC MEAN DISTANCE[26]

The following list of formulas contains those for most of the combinations of points and narrow rectangles likely to be needed in computing the inductance of shunts formed of manganin strips and

[26] The author is deeply indebted to Prof. F. W. Grover for his painstaking care in verifying these formulas.

small potential leads. They may be derived as special cases of the more general expression for the geometric mean distance of two symmetrically located rectangles of any thickness given by Rosa [27] but are more readily arrived at by the direct integration of the equation which defines geometric mean distance.

For the case of strips which have a thickness, d, very small compared to their width, w, Taylor's theorem may be applied and a power series in $\frac{d^2}{w^2}$ obtained. The first term of this series is given in each of the equations listed below.

If the geometric mean distances for pairs of lines or points and lines are desired, they can be obtained by merely omitting from the equations given below those terms which contain $\frac{d^2}{w^2}$ as a factor.

The formulas given here cover only those cases in which the rectangles (or lines) are equal and are placed with their longer axes parallel and with their shorter axes in the same straight line. The following notation is used:

w = length of rectangle (that is, width of strip).

d = width of rectangle (that is, thickness of strip).

g = distance between centers of rectangles.

a = coordinate of point from center of rectangle measured along shorter axis.

b = coordinate of point from center of rectangle measured along longer axis.

$n = \frac{1}{2} - \frac{b}{w}$.

D = geometric mean distance.

I. *Point from narrow rectangle*

(*a*) General case:

$$\log_e D = \frac{1}{2}\left(\frac{b}{w}+\frac{1}{2}\right)\log_e\left\{a^2+\left(b+\frac{w}{2}\right)^2\right\} - \frac{1}{2}\left(\frac{b}{w}-\frac{1}{2}\right)\log_e\left\{a^2+\left(b-\frac{w}{2}\right)^2\right\} - 1 + \frac{a}{w}\left\{\tan^{-1}\left(\frac{b}{a}+\frac{w}{2a}\right)-\tan^{-1}\left(\frac{b}{a}-\frac{w}{2a}\right)\right\} - \frac{d^2}{24w}\left\{\frac{\frac{w}{2}-b}{a^2+\left(\frac{w}{2}-b\right)^2}+\frac{\frac{w}{2}+b}{a^2+\left(\frac{w}{2}+b\right)^2}\right\}$$

(*b*) Symmetrical case, point on prolongation of minor axis of rectangle:

[27] B. S. Bull., 3, p. 6, 1907; B. S. Sci., Paper No. 47.

$$\log_e D=\frac{1}{2}\log_e\left(a^2+\frac{w^2}{4}\right)-1+\frac{2a}{w}\tan^{-1}\frac{w}{2a}-\frac{d^2}{24\left(a^2+\frac{w^2}{4}\right)}$$

(*c*) Point close to rectangle (but not symmetrical; that is, expansion in $\frac{a}{w}$); let $n=\frac{1}{2}-\frac{b}{w}$:

$$\log_e D=\log_e w+n\log_e n+(1-n)\log_e(1-n)-1$$
$$+\frac{\pi a}{w}-\frac{a^2}{2n(1-n)w^2}-\frac{d^2}{24w^2\,n\,(1-n)}$$

unless $b=\pm\frac{w}{2}$, in which case

$$\log_e D=\log_e w-1+\frac{\pi a}{2w}-\frac{a^2}{2w^2}-\frac{d^2}{24\,(w^2+a^2)}$$

(*d*) Point very distant from rectangle (that is, expansion in $\frac{w}{a}$):

$$\log_e D=\log_e a+\frac{\{n^3+(1-n)^3\}w^2}{6a^2}-\frac{\{n^5+(1-n)^5\}w^4}{20a^4}\cdots$$
$$-\frac{d^2}{24w^2}\left\{\frac{w^2}{a^2}-\frac{(1-3n+3n^2)\,w^4}{a^4}\right\}$$

(*e*) Point near and on prolongation of shorter axis of rectangle (that is, $b=0$, expansion in $\frac{a}{w}$):

$$\log_e D=\log_e w-1-\log_e 2+\frac{\pi a}{w}-\frac{2a^2}{w^2}-\frac{d^2}{6w^2}\cdots$$

(*f*) Point distant from rectangle and on prolongation of shorter axis (that is, $b=0$, expansion in $\frac{w}{a}$)

$$\log_e D=\log_e a+\frac{w^2}{24a^2}\cdots-\frac{d^2}{24w^2}\left\{\frac{w^2}{a^2}-\frac{w^4}{4a^4}\cdots\right\}$$

II. *Two rectangles*

(*a*) General case of equal, symmetrically placed, narrow rectangles (that is, expansion in $\frac{d}{w}$):

$$\log_e D=\frac{1}{2}\left(1-\frac{g^2}{w^2}\right)\log_e(g^2+w^2)+\frac{g^2}{w^2}\log_e g-3/2$$
$$+\frac{2g}{w}\tan^{-1}\frac{w}{g}+\frac{d^2}{12w^2}\log_e\frac{g^2}{g^2+w^2}\cdots$$

(*b*) Rectangles close together (that is, expansion in g/w):

$$\log_e D = \log_e w - \frac{3}{2} + \frac{g^2}{w^2}\log_e \frac{g}{w} + \frac{\pi g}{w} - \frac{3}{2}\frac{g^2}{w^2} + \frac{d^2}{12w^2}\left\{-\frac{g^2}{w^2} + \frac{g^4}{2w^4} \cdots + 2\log_e \frac{g}{w}\right\}$$

(*c*) Rectangles far apart $\left(\text{that is, expansion in } \frac{w}{g}\right)$:

$$\log_e D = \log_e g - \frac{w^2}{12g^2} + \frac{w^4}{60g^4} + \frac{d^2}{12w^2}\left\{-\frac{w^2}{g^2} + \frac{w^4}{2g^4} \cdots\right\}$$

(*d*) Rectangles coinciding (that is, g. m. d. of rectangle from itself):

1. For any rectangle:

$$\log_e D = \log_e \sqrt{w^2+d^2} - \frac{1}{6}\frac{d^2}{w^2}\log_e \sqrt{1+\frac{w^2}{d^2}} - \frac{1}{6}\frac{w^2}{d^2}\log_e \sqrt{1+\frac{d^2}{w^2}} + \frac{2}{3}\frac{d}{w}\tan^{-1}\frac{w}{d} + \frac{2}{3}\frac{w}{d}\tan^{-1}\frac{d}{w} - \frac{25}{12}$$

2. For narrow rectangle $\left(\text{that is, expansion in } \frac{d}{w}\right)$:

$$\log_e D = \log_e w - \frac{3}{2} + \frac{\pi d}{3w} + \frac{d^2}{6w^2}\log_e \frac{d}{w} - \frac{25d^2}{72w^2} \cdots$$

3. For line of length w (that is, $d=0$):

$$\log_e D = \log_e w - \frac{3}{2}$$

WASHINGTON, July 19, 1929.

THE EFFECT OF LIGHT ON SILVER CHLORIDE IN CHEMICAL ANALYSES

By G. E. F. Lundell and J. I. Hoffman

ABSTRACT

The experiments described in this paper show the direction and magnitude of the errors that may be expected in analytical work if silver chloride is not protected from light. Exposure to light during precipitation always causes positive errors if silver is in excess, and negative errors if hydrochloric acid is in excess. Exposure of dry precipitates has very little effect. The error, if any, is negative and becomes greater if the dried precipitate is moistened before exposure or if the precipitate is exposed before drying. Exposure to light probably produces a mixture of metallic silver and silver chloride.

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I. INTRODUCTION

In practically all analytical procedures dealing with the precipitation of silver chloride the analyst is cautioned to protect the precipitate from light. No information appears to be available, however, in regard to the magnitude of the errors caused by the neglect of such protection. The determination of silver or chlorine as silver chloride enters into so many fundamental analyses that it seemed advisable to study and record the effect of light. The experiments were performed from the standpoint of analytical chemistry rather than photochemistry.

II. EXPERIMENTAL

1. STANDARD SOLUTIONS USED

A dilute solution of hydrochloric acid was standardized in three ways: (1) By carefully precipitating and weighing silver chloride with every protection against light; (2) by titrating against a solution of sodium hydroxide which had been standardized (*a*) against the Bureau of Standards Standard Acid Potassium Phthalate No. 84, and (*b*) against the Bureau of Standards Standard Benzoic Acid No. 39b. The results of the three methods of standardization agreed within 1 part in 4,000.

Two solutions containing silver were used. The one was prepared by using as a standard, silver phosphate made according to the directions of Baxter and Jones [1] in their work on the atomic weight of phosphorus. The other was a 0.2 *N* solution of silver nitrate standardized by precipitating the silver as chloride with every protection against the influence of light. Weight burettes were used throughout, except for measuring the solution of silver nitrate in experiments 1 to 8, inclusive, Table 1. In these experiments carefully calibrated volume pipettes were used.

2. PRECIPITATION OF SILVER CHLORIDE

Two distinct series of precipitations were made. In both of these the conditions usually prescribed for precipitating silver chloride were maintained with the exception of the exposure to light. In the one series (Nos. 1 to 15 in Table 1) the silver in measured portions of the standard solutions was precipitated with such an excess of hydrochloric acid that the solution contained finally 1 ml of hydrochloric acid (specific gravity 1.19) per 100 ml of solution. In the other series chlorine was precipitated from weighed portions of the standard solution of hydrochloric acid by adding a few drops of nitric acid and an excess of silver nitrate in the amounts shown in Table 1. In all cases the precipitant was added slowly and with constant stirring. The final volume of the solutions was 200 ml, and all of the precipitates, excepting those in experiments 12, 13, 14, and 15 in Table 1, were coagulated by digesting on the steam bath for 15 to 30 minutes before they were exposed to light. The precipitates were caught in platinum crucibles fitted with platinum pads (Munroe crucibles). Those formed in the presence of an excess of hydrochloric acid were washed with a 1 per cent solution of hydrochloric acid (1 ml of HCl, specific gravity 1.19, per 100 ml of wash solution); those formed in the presence of an excess of silver nitrate were washed with a 0.5 per cent solution of nitric acid (1 ml of HNO_3, specific gravity 1.42, per 200 ml of wash solution). The washed precipitates were then dried at 130° to 140° C. and weighed.

3. EXPOSURE TO LIGHT

The results shown in Table 1 were obtained by exposing the precipitates in the precipitating medium in Pyrex beakers to light as indicated. The beakers exposed to north light were placed next to the north wall of the laboratory in such a position that no direct or reflected rays of the sun could reach them. Those exposed to artificial light were placed about 40 cm from an inclosed type carbon arc light, operated at 200 volts d. c. at 13 amperes, described by Walker and Hickson.[2]

---

[1] G. P. Baxter and G. Jones, J. Am. Chem. Soc., **32**, p. 298; 1910.
[2] P. H. Walker and E. F. Hickson, Ind. & Eng. Chem., **20**, p. 591; 1928.

TABLE 1.—*Effect of light on silver chloride in the precipitating medium*

No.	AgCl			Method of precipitation	Degree and kind of exposure
	Calculated	Found	Error		
	g	*g*	*g*		
1	1.3971	1.3948	−0.0023	Standard solution of $AgNO_3$, treated with an excess of HCl.	7 hours north light, occasional stirring.
2	1.3348	1.3216	−.0132	....do....	72 hours north light, 7 hours direct sunlight, occasional stirring.
3	.8293	.8176	−.0117	....do....	Do.
4	1.3971	1.3932	−.0039	....do....	2 hours direct dim sunlight, constant stirring.
[1] 5	.6985	.6947	−.0038	....do....	Do.
6	1.3971	1.3915	−.0056	....do....	2 hours direct dim sunlight, no stirring.
[1] 7	.6985	.6938	−.0047	....do....	Do.
8	1.3971	1.3883	−.0088	....do....	5 hours arc light, occasional stirring.
[2] 9	.7859	.7851	−.0008	....do....	2 hours in bright laboratory, no direct or reflected sunlight, occasional stirring.
[2] 10	.6961	.6954	−.0007	....do....	Do.
[2] 11	.0279	.0278	−.0001	....do....	Do.
[3] 12	.0028	.0022	−.0006	Very faint excess of HCl during time of exposure to light. Acid concentration raised to 1 per cent by volume before filtration.	3 hours dim sunlight+20 hours arc light.
[3] 13	.0028	.0022	−.0006	....do....	Do.
[3] 14	.0028	.0029	+.0001	....do....	Protected from all light.
[3] 15	.0028	.0028	.0000	....do....	Do.
16	.6683	.6717	+.0034	Standard solution of HCl treated with 100 per cent excess of $AgNO_3$.	7 hours north light, occasional stirring.
17	.6669	.6751	+.0082	....do....	2 hours direct dim sunlight, constant stirring.
[1] 18	.7429	.7554	+.0125	....do....	Do.
19	.7683	.7771	+.0088	....do....	2 hours direct dim sunlight, no stirring.
[1] 20	.6410	.6476	+.0066	....do....	Do.
21	.7921	.8271	+.0350	....do....	5 hours arc light, occasional stirring.
22	1.1967	1.2506	+.0539	Standard solution of HCl treated with 1 to 3 ml of a 0.2 *N* solution of $AgNO_3$ in excess.	72 hours north light+7 hours direct sunlight, occasional stirring.
23	1.2903	1.3179	+.0276	....do....	5 hours direct sunlight, occasional stirring.
24	1.2762	1.3097	+.0335	....do....	Do.
[2] 25	.5184	.5194	+.0010	....do....	2 hours in bright laboratory, no direct or reflected sunlight, occasional stirring.
[2] 26	.5696	.5706	+.0010	....do....	Do.

[1] The exposure of Nos. 5, 7, 18, and 20 was exactly the same.

[2] Results Nos. 9, 10, 11, 25, and 26 were obtained by the use of weight burettes, and the figures given in the "calculated" column were obtained under exactly the same conditions as those in the "found" column, excepting that those in the "calculated" column were protected from all light, while those in the "found" column were exposed as indicated.

[3] Nos. 14 and 15 received exactly the same treatment as Nos. 12 and 13 excepting the exposure to light. Total loss of chlorine in Nos. 12 and 13 would have amounted to 0.0007 g.

The results shown in Table 2 were obtained by exposing the precipitates on perforated platinum crucibles fitted with platinum pads. The sources of light were the same as described in the previous paragraph.

TABLE 2.—*Effect of light on silver chloride in the crucible*

No.	Weight of normal precipitate of AgCl before exposure	Weight after exposure	Error	Treatment of precipitate before exposure	Degree and kind of exposure
	g	*g*	*g*		
1	0.7844	0.7840	−0.0004	Dried at 130° C.	16 days north light plus 7 hours direct sunlight.
2	.7645	.7642	−.0003	do	Do.
3	1.2506	1.2504	−.0002	do	Do.
4	.8379	.8378	−.0001	do	2 hours direct sunlight.
5	1.3876	1.3873	−.0003	Dried at 130° C. and then moistened.	Do.
6	.8212	.8203	−.0009	do	2 hours arc light.
7	[1] .6985	.6973	−.0012	Filtered and washed, but not dried prior to exposure to light.	Do.
8	[1] .6985	.6958	−.0027	do	5 hours arc light.

[1] This represents the weight of AgCl which should have been obtained under normal conditions as calculated from the standard solution used.

III. DISCUSSION OF RESULTS

No analyst would expose silver chloride to an arc light or direct sunlight in determinations of silver or chloride. The results so obtained serve only to show the direction and magnitude of the error. Results Nos. 1, 9, 10, 11, 16, 25, and 26, in Table 1, however, are such as might be obtained in ordinary analytical work. Results Nos. 1 and 16 were obtained by precipitating at 5 p. m. and allowing the solution to stand unprotected in north light until the next morning at 9 o'clock. The error in both cases is significant. Results Nos. 9, 10, 11, 25, and 26 were obtained by performing the following operations in a bright laboratory, but not in direct or reflected sunlight. The silver chloride was precipitated in the usual manner, digested on the steam bath for 30 minutes, and set aside for one hour. The cool solution was then filtered and the precipitate washed with a 1 per cent solution of hydrochloric acid, dried at 130° to 140° C., and weighed. The total time required for the determination, including the drying and weighing, was about three hours, and the results represent what can be expected if determinations are made with no other precautions than the avoidance of sunlight. [3] The errors (approximately 1 part per 1,000 in the precipitation of silver and 2 parts per 1,000 in the precipitation of hydrochloric acid) are what can be expected in standardizations of 0.1 *N* solutions, and are too large to be ignored in analyses that lay claim to accuracy.

The action of light always causes low results if silver chloride is formed by adding an excess of hydrochloric acid to a solution of silver; it always causes high results if silver chloride is formed by adding an excess of silver nitrate to a solution of hydrochloric acid or a chloride. The positive error is always greater than the negative for the same degree of exposure.

Both errors are caused by the decomposition of silver chloride. Little or none of the chlorine resulting from the decomposition

[3] For example, in one text it is stated: "Die ganze Operation der Silberbestimmung kann unbeschadet der Genauigkeit bei gewöhnlichen Tageslicht gemacht werden."

escapes but is largely changed back into chloride ions.[4] If hydrochloric acid is in excess, the chlorine resulting from the decomposition of silver chloride is not reprecipitated because no more silver ions are available. The error, therefore, is negative and represents the quantity of chlorine lost by the precipitate. If, however, the chloride ion is precipitated by an excess of silver nitrate, the chlorine resulting from the decomposition is reprecipitated as silver chloride. The error in this case is positive because some of the chloride ions precipitate more than one ion of silver. The positive error is further increased by the fact that the decomposition of silver chloride by light is accelerated by the presence of silver nitrate.[5] If ideal conditions prevail the reactions might proceed until the excess of silver nitrate in solution would be exhausted. In this case the excess would determine the extent of the plus error. If exposure were continued after the excess of silver nitrate was used up, the precipitate would begin to lose weight, but never (assuming quantitative conversions) below the theoretical unless the weight of silver in the silver nitrate added in excess during the precipitation was less than the original weight of chlorine in the solution.

The results shown in Table 2 indicate that the effect of light on dry precipitates of silver chloride will cause only very small negative errors. These errors become greater if the dry precipitates are moistened and then exposed to the action of light. The effect of light seems to be still greater if the precipitates are filtered, washed, and exposed before drying. Precipitate No. 6, in Table 2, was washed with 100 ml of water after it had been exposed to light, dried, and weighed. The washing caused a loss in weight of 0.3 mg in addition to the 0.9 mg previously lost. The washings showed no silver, but gave a faint test for chloride. The other precipitates in Table 2 lost no more than 0.1 mg as a result of a similar washing after they had been exposed to light and dried.

IV. EXAMINATION OF THE PRECIPITATES FORMED UNDER THE INFLUENCE OF LIGHT

All precipitates formed under the influence of light showed an increased weight if silver nitrate was in excess and a deficiency in weight when hydrochloric acid was in excess. It would be difficult to determine the composition of such precipitates by chemical analysis. In a precipitation of silver with an excess of hydrochloric acid under the influence of light a solution equivalent to 0.6985 g of silver chloride yielded only 0.6858 g. No silver was left in the filtrate. When the precipitate was treated in a porcelain crucible with concentrated nitric acid and then repeatedly with hydrochloric acid to convert all silver to silver chloride, a final weight of 0.6983 g was obtained. This can be explained by assuming that the original precipitate consisted of a mixture of metallic silver and silver chloride and that

[4] The conversion is not necessarily quantitative. For a discussion on the change of chlorine to chloride ions in dilute acid solutions under the influence of light, see A. J. Allmand, P. W. Cunliffe, and R. E. W. Maddison, J. Chem. Soc., **127**, p. 822; 1925, and p. 655; 1927.

[5] J. M. Eder, Ausführliches Handbuch der Photographie, **4**, pt. 1, p. 12, 2d ed.; 1898.

the treatment with nitric and hydrochloric acids converted all of the silver to chloride.[6]

In a precipitation of hydrochloric acid with an excess of silver nitrate under the influence of light a solution equivalent to 0.8887 g of silver chloride yielded 0.9232 g. By treating this precipitate with concentrated nitric acid and then with hydrochloric acid in a porcelain crucible a final weight of 0.9342 g was obtained. If it is assumed that the original precipitate (0.9232 g in weight) consisted of metallic silver and silver chloride, then the excess weight (0.9232 g − 0.8887 g or 0.0345 g) should be the weight of metallic silver. This is equivalent to 0.0113 g of chlorine and should correspond to the increase in weight when the precipitate was treated with nitric and hydrochloric acids. The actual increase in weight was 0.9342 g − 0.9232 g or 0.0110 g.

Neither of these results definitely eliminates silver subchloride, Ag_2Cl, as a constituent of the precipitates. By working with thin films and a microbalance Hartung [7] observed a decomposition of silver iodide under the influence of light amounting to as much as 90 per cent. Others [8] have shown that from the standpoint of photography synthetic mixtures of colloidal silver and silver halides react the same as photohalides formed under the influence of light. Experiments Nos. 12, 13, 14, and 15, in Table 1, were performed to see whether the decomposition of silver chloride could be pushed beyond the point represented by the formula Ag_2Cl. In these tests so little silver chloride was involved that no precipitate settled from the cool opalescent solution until it had been exposed to the light for over five hours. The results show that almost all of the chlorine was lost, and indicate that metallic silver will finally be obtained if the particles of silver chloride are very small and the exposure is sufficiently prolonged.

V. SUMMARY

The experiments described in this paper show the direction and magnitude of the errors that may be expected in analytical work if silver chloride is not protected from light during precipitation, filtration, and drying. Exposure to light during precipitation always causes positive errors if silver is in excess and negative errors if hydrochloric acid is in excess. Light has very little effect on dry silver chloride. The error, if any, is negative and becomes greater if the dried precipitate is moistened before exposure. It is still greater if the precipitate is exposed without previous drying. The precipitate obtained during exposure to light probably consists of a mixture of metallic silver and silver chloride.

WASHINGTON, September 27, 1929.

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[6] In the preparation of silver phosphate, Baxter and Jones (see footnote 1, p. 110) observed that a residue was left if the salt was dissolved in dilute nitric acid. This insoluble residue was greater in samples from which light was not excluded during the preparation. Analyses indicated that it was metallic silver.

[7] E. J. Hartung, J. Chem. Soc., p. 1349; 1926.

[8] Lüppo-Cramer Kolloidchemie und Photographie, 2d. ed.; 1921.

METHOD AND APPARATUS USED IN TESTING PIEZO OSCILLATORS FOR BROADCASTING STATIONS

By E. L. Hall

ABSTRACT

Piezo oscillators are the most suitable frequency standards thus far devised for use in radio broadcasting stations. A piezo oscillator may be used either to check the frequency of the station or to control its frequency. Most of the piezo oscillators tested by the bureau are for use in checking the frequency of the station. Piezo oscillators are capable of high precision in the measurement of their frequency if a beat note is produced by adjusting another generator to a similar frequency. This principle is employed in the methods and apparatus described in the paper.

After preliminary tests to determine the suitability of the quartz plate and its fundamental frequency, the piezo oscillator is kept in a temperature-controlled room for not less than two days, during which frequency measurements are made.

The method consists in measuring the frequency of the piezo oscillator under test in terms of a 200 kc temperature-controlled piezo oscillator. This is accomplished by adjusting a radio-frequency generator to the frequency which the piezo oscillator under test should have. This adjustment is made by using harmonics from a 10 kc generator which is kept accurately set in terms of the 200 kc standard by observing a special form of beat indicator. The frequency difference between the test piezo oscillator and the generator set in terms of the standard is measured by comparison with an audio-frequency generator. A frequency meter of special design is used to check the frequency difference and determine the sign of the correction to be applied. The method described is also useful in the calibration of frequency meters and the measurement of station frequencies.

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I. PIEZO OSCILLATORS AS FREQUENCY STANDARDS FOR BROADCASTING STATIONS

A broadcasting station, to maintain its assigned frequency, must be provided with an accurate frequency standard. A piezo oscillator is the most suitable frequency standard thus far devised. It is

a generator of radio-frequency current, the frequency of which is determined primarily by the dimensions of the quartz plate used. The bureau's service to the broadcasting stations consists of measuring the frequency of the piezo oscillator, or adjusting the quartz plate so that the piezo oscillator has the frequency to which the station is assigned, and issuing a test certificate. This service is one of the classes of radio tests undertaken by the bureau.

A piezo oscillator may be used in either of two ways in maintaining a station on its assigned frequency; first, it may be used for checking the frequency of the station; second, it may be used to control the frequency of the station. Tests at the bureau are usually limited to piezo oscillators intended for use in the first way mentioned because of the practical difficulties in submitting a complete piezo oscillator intended to control the frequency of the station. If the broadcasting station uses a piezo oscillator which is maintained at a constant temperature, the complete temperature-control equipment should be submitted with the piezo oscillator so that the test can be conducted at the desired temperature and under the conditions of use.

The bureau will undertake to adjust a piezo oscillator to the frequency of a station if the frequency as received is not more than 1 per cent below that desired, but will not accept it for adjustment if the frequency is above that desired. Experience in adjusting quartz plates by grinding demonstrates that no guarantee can be made of obtaining satisfactory results. This frequency adjustment is the final step in a series of operations which are required in a technical manufacturing process. Data taken by the Bureau of Standards and other laboratories on the behavior of quartz plates as their dimensions are changed, show that there is a small probability of obtaining a suitable frequency standard by submitting a single quartz plate for adjustment, and this type of test is not encouraged. A more satisfactory type of test, both from the standpoint of the bureau and the station, is to measure the frequency of a piezo oscillator which has been completed and adjusted to frequency by the manufacturers and which operates initially in a satisfactory manner.

II. TESTING METHOD

While the apparatus and method of use reported herein were developed with the idea of applying them to the testing of piezo oscillators having frequencies within the broadcasting band, it was found that the system could be applied with considerable advantage to other tests, such as the measurement of the frequencies of broadcasting stations and the calibration of frequency meters.

A test method and the standards used in calibration work should be capable of a precision at least ten times that of the apparatus to be tested. The precision with which a given adjustment of the apparatus under test can be reproduced should be a guide as to the precision and accuracy of the system to be employed in the test. As the system of measurement to be described is capable of a precision of setting of better than 1 part in 1,000,000, it would be a waste of effort, for example, to use the system to its limit in testing a commercial frequency meter which is only capable of setting to 1 part in 5,000. Piezo oscillators are capable of high precision of measurement, but the fact that an extremely precise measurement of the frequency of the piezo oscillator can be made gives no indication whether the device

will be a satisfactory frequency standard for a broadcasting station. Such precise measurement, however, enables one to determine how much the frequency of the piezo oscillator is changed by varying the conditions of operation, and hence to estimate its ability to maintain its frequency after shipment.

As the high precision possible in measurements of the frequency of piezo oscillators depends upon measurement of frequency differences, a brief discussion of how the frequency differences are produced may assist in a better understanding of the paper by those not familiar with such measurements. In any type of radio-frequency generator the greatest amount of power available is present at the fundamental frequency, which depends upon the value of the inductance and capacity of the resonant circuit. Power is also present at other frequencies which are integral multiples of the fundamental frequency. Although the power available at the harmonic frequencies is very small and decreases as the harmonic number increases, yet it is suffi-

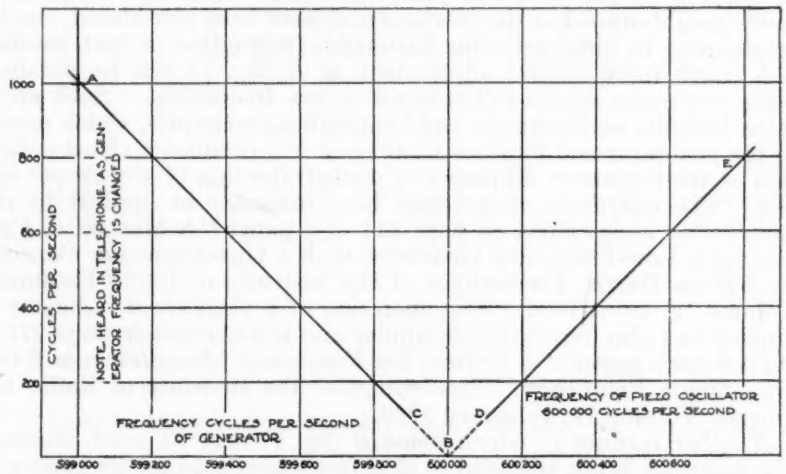

FIGURE 1.—*Beat note produced between piezo oscillator and a radio-frequency generator whose frequency may be changed*

cient to operate a sensitive device, such as a telephone receiver. By means of suitable amplification, harmonics as high as the two-hundredth and higher may be employed in measurements.

If a piezo oscillator having a fundamental frequency of 600 kc is assumed to be in operation, loosely coupled to a radio-frequency generator operating at 599 kc, telephone receivers suitably connected to the piezo oscillator or generator will give an audible response or musical note of 1 kc (1,000 cycles), as shown at *A* in Figure 1. The 1,000-cycle note is the difference in frequency between the radio-frequency generator operating at 599,000 cycles per second and the piezo oscillator operating at 600,000 cycles per second. If the frequency of the generator is gradually increased, as represented by line *AB* (fig. 1), the difference in frequency between it and the piezo oscillator becomes less, and, consequently, the audible note heard in the telephone receivers becomes lower. As the frequency of the generator is slowly increased by turning a condenser dial, a setting of the condenser will be reached corresponding to point *C* (fig. 1),

where the telephone receiver is silent, because the frequency is below audibility. If this dial setting is noted and the dial turned slowly in the same direction as before, it may be found that the telephones do not give a response over a certain number of divisions change on the dial until a frequency represented by point D (fig. 1) is reached. This condition of silence in the telephones is often referred to as "zero beat," because the impulses or beats in the telephones can not be heard for they are below audibility. While the lower limit of audibility is usually taken as 16 cycles per second, the average telephone receiver will not respond to so low a frequency. For the purpose of clearness in Figure 1, and to emphasize the fact that a zero-beat adjustment is not precise, the lines AB and BE are shown dotted near their lower ends, indicating no response in the telephones, although the region of zero beat is usually more definite than indicated. A further increase in the frequency of the generator from point D toward E (fig. 1) increases the frequency difference or beat frequency between generator and the piezo oscillator. Although frequencies in the neighborhood of the fundamental have been considered, similar results may be obtained using harmonics from either or both sources.

A much more precise adjustment at B (fig. 1) can be obtained using apparatus which will respond to low frequencies. Such apparatus includes oscillographs and beat-indicator circuits, which couple to the generator and piezo oscillator and will produce a visual indication of the frequency difference of a small fraction of a cycle per second. The operation of a visual beat indicator as applied to low frequencies is described on page 214 of a paper "A Method of Calibrating a Low-Frequency Generator with a One-Frequency Source," by Sylvan Harris, Proceedings of the Institute of Radio Engineers, Volume 14, April 1926. The operation of a visual-beat indicator as applied to radio frequencies is similar and is described on page 275 of the author's paper, "A System for Frequency Measurements Based on a Single Frequency," Proceedings of the Institute of Radio Engineers, Volume 17, February 1929.

Another manner in which point B (fig. 1) may be used although the generator is not adjusted to that frequency, is to set the generator to such a frequency that the frequency difference between it and the piezo oscillator operating at point B is equal to the known frequency of a tuning fork. Harmonics of the tuning fork may be used, depending upon the ability of the operator to distinguish differences in the pitch of two notes. An operator having a "musical ear" can readily use this method, although results obtained by an operator not so gifted might be unreliable.

A very precise adjustment of the generator at the frequency corresponding to point B (fig. 1) can also be obtained by employing another radio-frequency generator, which is operated at some frequency having a harmonic within, for example, 500 to 1,500 cycles per second of the frequency at B. This method has been described on page 28 of an article "Frequency Standardization," by J. K. Clapp, Journal of the Optical Society of America and Review of Scientific Instruments, Volume 15, 1927.

The circuits employed in the testing of piezo oscillators make use of the principles outlined in the above paragraphs.

As the piezo oscillators to be tested are capable of precise measurement, it becomes necessary to use a standard for the testing work

whose frequency is accurately known and maintained constant. The choice for the standard was a piezo oscillator which operates under constant conditions as to temperature and voltages applied. Its frequency is checked at least once a week by intercomparison with other temperature-controlled piezo oscillators. The frequencies of all piezo oscillators for broadcasting stations are referred to this one standard by means of the apparatus described below.

As the piezo oscillators to be tested for broadcasting stations have frequencies which are multiples of 10, beginning at 550 kc and ending with 1,500 kc, a system giving frequencies spaced 10 kc apart is convenient for test purposes. A 10 kc generator was accordingly made a part of the apparatus and is precisely adjusted to 10 kc. It is, in fact, manually controlled and slightly readjusted when necessary, rather than automatically held at 10 kc. The reason for this arrangement is that it may be desirable to set the 10 kc generator to some other frequency, such as 15, 25, 50, or 100 kc, when used in other

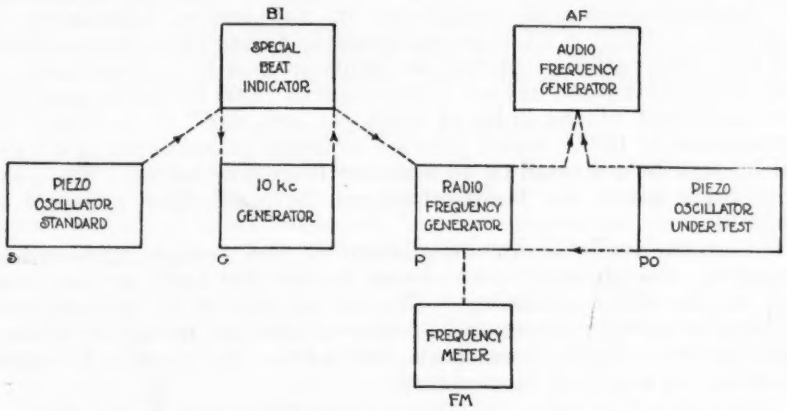

FIGURE 2.—*Apparatus used in testing piezo oscillators for broadcasting stations*

The dotted arrows indicate how the various pieces of apparatus work with the remainder of the equipment.

measurement work, in which case the harmonics would be spaced farther apart and would be of a lower order and, consequently, stronger. This permits a great extension of the frequency range of the system. The same piezo oscillator can be used and the generator will give harmonics spaced at almost any desired intervals, thus providing a very flexible system.

It should also be pointed out that a piezo oscillator of almost any value can be selected and used as the standard in a manner similar to that here described. The harmonics obtained may not be convenient decimal values, but calculations can always be made and the usefulness of any piezo oscillator greatly extended.

The system herein described is best explained by reference to Figure 2, which shows schematically the apparatus as used. The system includes: A temperature-controlled piezo oscillator, *S*, the frequency of which is accurately known, in terms of which the measurements are made; a 10 kc vacuum tube generator *G*, capable of very precise frequency control, and giving a very constant fre-

quency; a radio-frequency vacuum tube generator P, covering the range of frequencies desired; the piezo oscillator to be calibrated, PO; a calibrated frequency meter FM, for determination of the order of the harmonics of the generator P in terms of generator G; a calibrated audio-frequency generator AF, capable of precise adjustment; a special form of combined beat indicator and generating detector BI, by means of which the operator maintains the various elements of the system in the frequency relationship desired. The method of operating the apparatus is given below.

III. DESCRIPTION OF APPARATUS

1. TEMPERATURE-CONTROLLED ROOM

Very few of the piezo oscillators submitted for test have been equipped with temperature-control apparatus for maintaining the quartz plate at a constant temperature. Prior to the installation of the temperature-control equipment in the testing laboratory, a variation of 20° C. in 24 hours was possible during the winter months and half this variation during the summer months. Considering a mounted quartz plate having a frequency of 1,000 kc and a temperature coefficient of the order of 0.003 per cent per ° C., a change in temperature of 10° C. would produce a change in frequency of 0.3 kc, which could be indicated on an ordinary frequency meter. The need for a room where the temperature can be maintained constant is evident.

The room available for installation of the temperature-control apparatus was about 21 feet square by 10½ feet high on the main floor of the Radio Building. The installation of a 2-horsepower cooling system for summer and a 5-kilowatt electric heater for winter, controlled by suitable thermostats, has enabled the room to be maintained at the required temperature.

2. FREQUENCY STANDARD

The standard in terms of which the frequencies of piezo oscillators are measured is a 200 kc temperature-controlled piezo oscillator. This type of piezo oscillator has been described by Worrall and Owens in an article entitled "The Navy's Primary Frequency Standard," in the Proceedings of the Institute of Radio Engineers, pages 778–793, volume 16, June, 1928. Some changes in the method of operation and use have been made. The piezo oscillator is inclosed in a specially constructed cabinet which is maintained by means of a mercury thermostat at such a temperature as to give a frequency of 200,000 cycles. This cabinet is located in the constant-temperature room. Heat is provided by means of electric lamps placed in the outer sides of the box, and the air is circulated by means of a fan. The thermostat is placed in the air stream in a position to give the most sensitive temperature control. Under usual conditions no change in the reading of a thermometer graduated in 0.1° C. can be observed.

3. GENERATORS

There are three different generators or oscillators required in the testing work: (1) A small generator which may be adjusted to 10 kc; (2) a generator covering the radio frequencies at which tests are to be

made, hereafter called the "power generator"; and (3) a generator of audio frequencies.

The 10 kc generator employs a 5-watt vacuum tube in a Hartley circuit in which a 2-plate variable air condenser permits very minute adjustments in frequency.

The power generator uses the tuned-plate circuit and a 250-watt tube with 600 volts on the plate. Slow-motion devices on the variable condensers permit the precise adjustment of the generator to the desired frequency. It is equipped with a condenser-switching mechanism which assists in rapidly obtaining zero beat with a piezo oscillator. This mechanism changes the frequency from a point above zero beat to a point below zero beat by operating a switch handle. When the note heard on either side of zero beat is the same, the midposition of the switch gives zero beat. This is accomplished by changing the variable condenser slightly.

The audio-frequency generator is a commercial product. The low frequencies are produced in a tuned-plate generating circuit using a 5-watt tube, and the output is amplified by another 5-watt tube. A filter circuit is provided so that the harmonics above various specified frequencies, as indicated by a switch, are reduced to a minimum.

4. SPECIAL BEAT INDICATOR

The special beat-indicator circuits used are the result of an attempt to make possible the precise adjustment of the frequency of one circuit to that of another and not have an interaction between them which may change the frequency of the standard. The beat-indicator circuits used not only accomplished the desired results, but were found to have other important uses in the measurement system.

Essentially, the beat-indicator circuit shown in Figure 3 is a generating-detector circuit. A 1,000-turn coil in the grid circuit couples to the 10 kc generator *G* and to the output of the piezo oscillator *S*. A 600-turn coil in the plate circuit couples to a coil of 8 or 10 turns in series with a crystal detector and direct current microammeter *A*, which gives the visible indication. An audio-frequency transformer is connected in the plate circuit as shown, and telephone receivers or a 2-stage amplifier may be connected to the secondary winding of the transformer as desired. A detector tube is at times connected in ahead of the 2-stage amplifier and serves to increase the sensitivity of the system. A small pick-up coil is sometimes connected to the input terminals of the detector tube, and serves to increase the coupling between the power generator and the 10 kc generator.

5. FREQUENCY METER OF HIGH RESOLVING POWER

In the course of the development and improvement of frequency standards and apparatus a few years ago, the need was felt for a frequency meter capable of more precise measurement and greater accuracy. About 1925 the frequency meter to be described was constructed, although an improvement in the method of resonance indication has recently been added. The frequency meter as originally constructed was found to be more than capable of the precision expected. It soon was found to be indispensable in frequency measurements made during the adjustment of quartz plates to a desired frequency, as requests for such work began to be received.

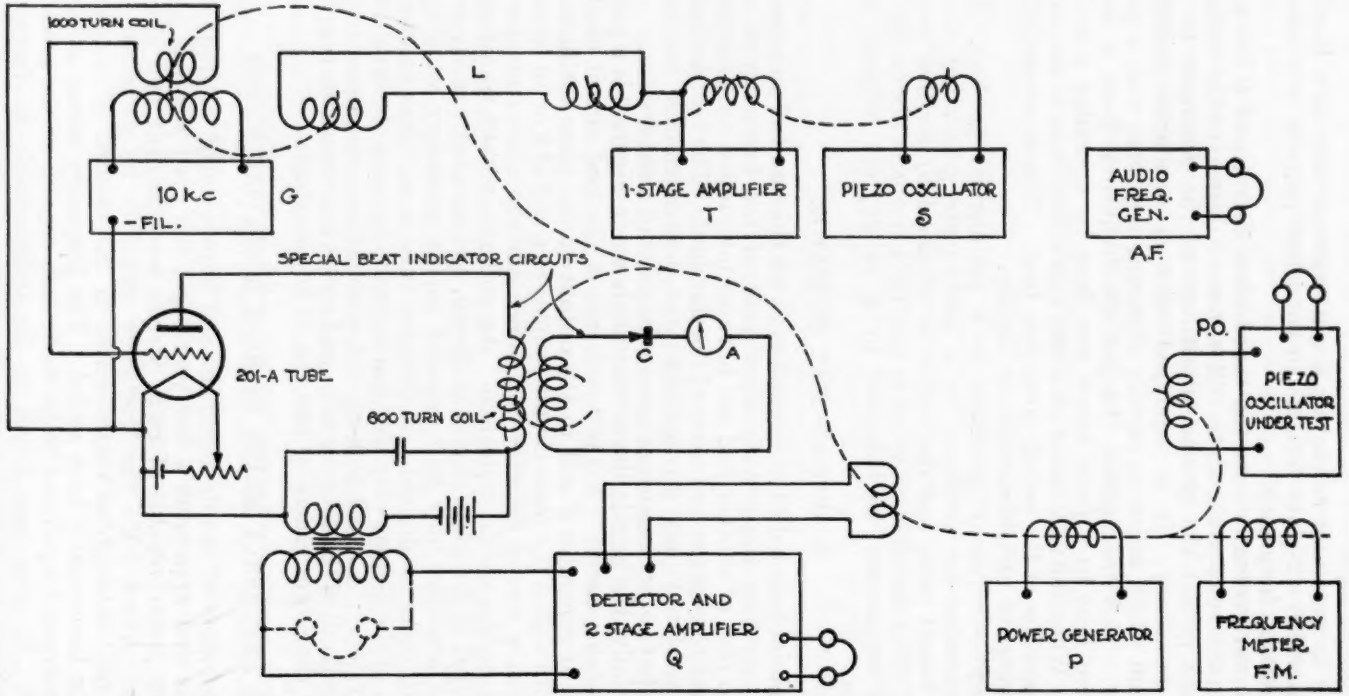

FIGURE 3.—*Schematic diagram of apparatus used in testing piezo oscillators, showing electromagnetic coupling between different units by dotted lines*

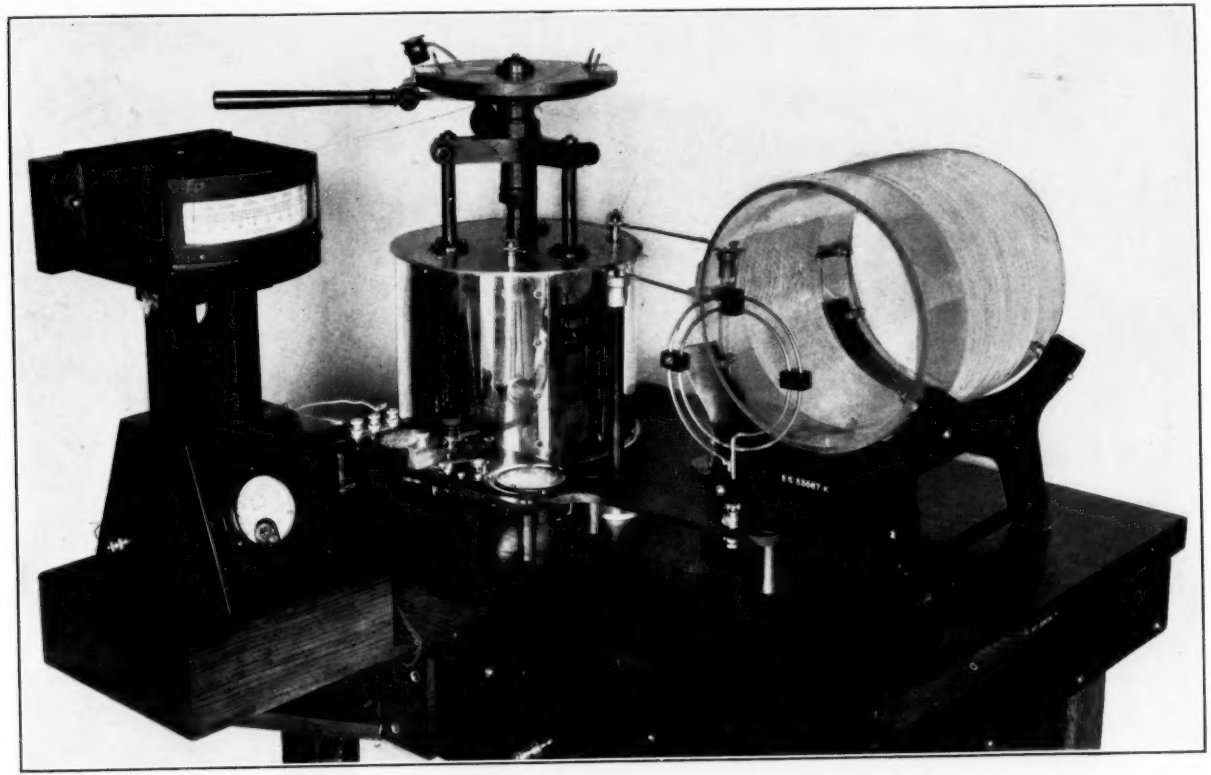

FIGURE 4.—*Special frequency meter used in measuring frequency differences*

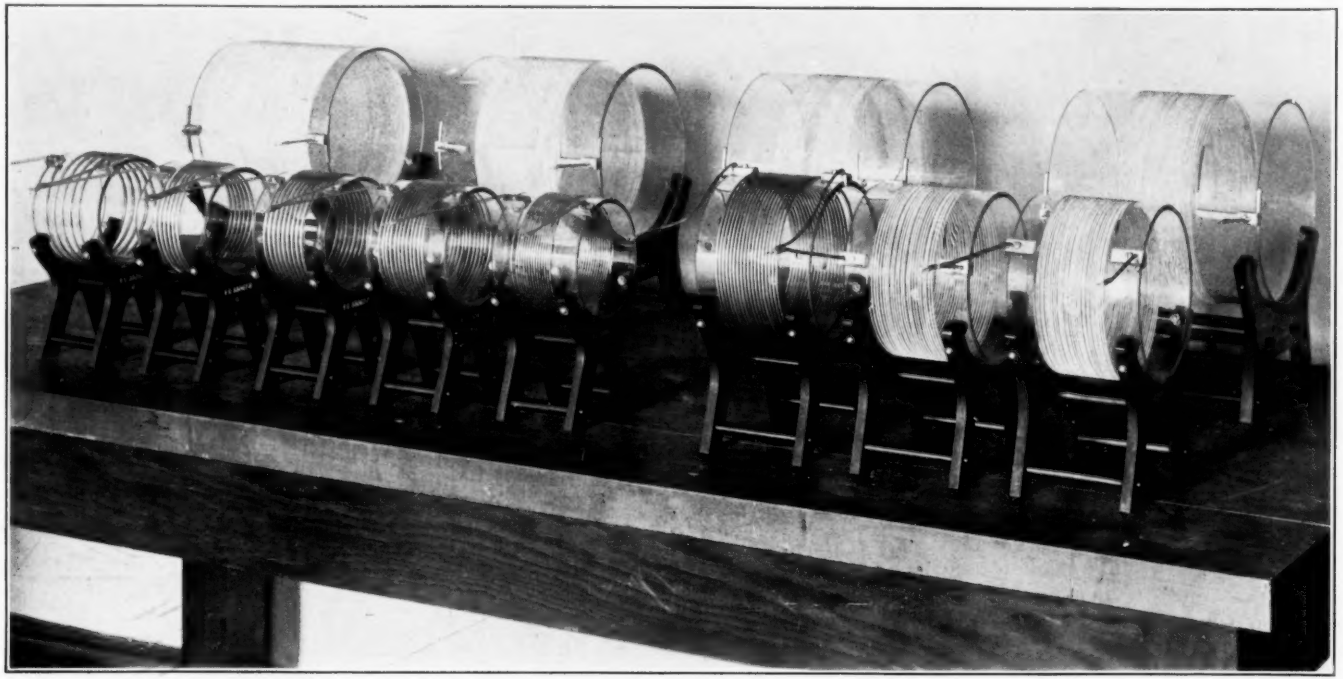

FIGURE 5.—*Series of inductors used on frequency meter shown in Figure 4*

Frequency range covered, 170 to 5,350 kc.

It is still in use for adjustment work or where small changes in frequency are to be measured.

The frequency meter is shown in Figure 4, and the series of coils for it is shown in Figure 5. The condenser is made up of two air condensers, one fixed and the other variable, mounted within the cylindrical shield. The condenser is provided with a special scale and vernier taken from a transit obtained from the United States Coast and Geodetic Survey. The scale is graduated throughout the circumference in sixths of degrees. With a vernier of 60 divisions it is possible to read a movement of 10 seconds of arc, or approximately 0.003°. This is much higher precision in scale reading than is necessary to obtain a fairly high degree of precision in frequency measurement. In practice it is convenient to use but 10 main divisions on the vernier, which means reading the condenser scale to approximately 0.016°. When such agreement in the condenser reading is obtained, the precision of the frequency measurement is 0.003 per cent.

The maximum capacity of the condenser is approximately 400 $\mu\mu$f, half of which is in the fixed portion. This gives a capacity variation of 200 $\mu\mu$f and a minimum capacity of 200 $\mu\mu$f. The movable plates of the condenser are so shaped as to give practically a straight-line percentage frequency curve and allow the same percentage accuracy of measurement at any part of the scale. Since the ratio of maximum to minimum capacity is about 2 to 1, the frequency ratio for any coil used with the condenser is $\sqrt{2}$.

The coils used with this frequency meter are wound on Pyrex glass cylinders. The glass forms were chosen as giving greater constancy and stability than was obtainable with a skeleton-frame inductor. The inductors were wound with different sizes of wire, as selected from the data reported in a previous paper by the author.[1]

The frequency meter has been used by adjusting the condenser to resonance, as indicated by the maximum deflection of a direct current microammeter in a separate series circuit containing a crystal rectifier and small coil of two turns coupled to the coil of the frequency meter. Recently an improvement in the precision of setting was obtained by incorporating an arrangement used by a manufacturer of radio apparatus and standards in some special frequency meters. A very small condenser was built into the condenser shield so that the total capacity could be slightly increased by connecting the condenser into the circuit, which is accomplished by means of a spring push button. The main condenser is so adjusted that the deflection of the microammeter is the same with or without the small condenser in the circuit. When the frequency meter is correctly adjusted it is not quite in resonance with the generator, but set to a somewhat higher frequency. The calibration is based on this setting.

6. AUXILIARY APPARATUS

Among the auxiliary apparatus used in the measurements, the most useful has been a set of tuning forks ranging in frequency from 100 to 2,000 cycles. By matching a beat note with the note of a tuning fork, a known frequency difference can be produced, which

[1] B. S. Tech. Paper No. 330, "Resistance of Conductors of Various Types and Sizes as Windings of Single-Layer Coils at 150 to 6,000 Kilocycles." Obtainable from Superintendent of Documents, Government Printing Office, Washington, D. C., for 5 cents.

permits a simple calculation of a frequency which may be inconvenient to set precisely otherwise. Three electrically driven forks have been available, but the simple type of fork held in the hand and struck with a small mallet has been found more convenient.

A detector and 2-stage amplifier has been very useful. A small coil coupled to both the piezo oscillator and the power generator is at times connected to the input of the detector circuit in order to amplify the beat frequency. Other apparatus, such as another radio-frequency generator and a two-string oscillograph, is sometimes useful in making measurements.

IV. OPERATION OF APPARATUS

1. ADJUSTMENT OF 10 KC GENERATOR IN TERMS OF PIEZO OSCILLATOR STANDARD BY MEANS OF SPECIAL BEAT INDICATOR

The approximate setting of the 10 kc generator G (fig. 3) is first found by listening in telephones connected in the output of the amplifier Q, which is connected to the special beat indicator. After adjusting the 10 kc generator G to zero beat a rather faint high note may be heard, or, if the power generator P (fig. 3) is operating near some harmonic of the 10 kc generator, rapid pulsations in the beat note between the two generators may be heard. This renders it much easier to adjust the 10 kc generator correctly. By careful adjustment of the tuning control of the 10 kc generator, this high note will fluctuate in intensity, and when the fluctuation becomes slow enough the pointer of the milliammeter A will be found to vibrate in step with the fluctuation. By further adjustment of the tuning control of generator G the pointer can be kept from moving. At this point the 10 kc generator G can be shifted by further slight adjustment so that there is either a high-pitched faint note or absolute quiet. The latter condition occurs when the generator is correctly adjusted with respect to the frequency standard used. If the generator gets out of adjustment by as much as one cycle per second in a minute the operator will detect it by hearing the high-pitched note appear in the telephones. Slight errors in this setting may not be important unless a high harmonic is to be used. Errors in adjustment of the order of a few hundredths of a cycle per second are immediately apparent and the 10 kc generator can be readjusted. The milliammeter A is used only to indicate the desired adjustment between the frequency standard S and generator G and never indicates the adjustment of generator P. A second indicator might be used for this purpose, but has not been incorporated thus far because of the added complication of the circuits.

The sensitiveness of the visible beat indicator is shown by the fact that when the coils of an unshielded piezo oscillator and the 10 kc generator were coaxial and from 2 to 3 feet apart, visible beats of the beat-indicator milliammeter, A (fig. 3), were readily obtained. Type 201–A tubes were used in both the piezo oscillator and the 10 kc generator. The link circuit L and the 1-stage amplifier T were not used in this case. In other words, the coupling to the piezo oscillator S was extremely loose, which meant that there was no danger of the frequency of the piezo oscillator, which was used as the standard, being changed by the other circuits. Thus the beat-indicator system could not affect the frequency of the standard.

2. ADJUSTMENT OF POWER GENERATOR TO DESIRED FREQUENCY BY MEANS OF AUDIBLE CHARACTERISTICS OF BEAT INDICATOR

When the 10 kc generator G has been adjusted accurately, the next step is to adjust the power generator P, (fig. 3) to the desired harmonic of the 10 kc generator. The telephones in the 2-stage amplifier Q, (fig. 3) also serve to indicate the correct adjustment of the power generator P. When working at the higher frequencies in the broadcast band, beat frequencies which otherwise would not be heard are made audible by placing a pick-up coil connected in series with the telephone leads in the vicinity of the power generator P.

The frequencies of the power generator P, in which the last digit is zero, give a zero beat which can not be set accurately by aural methods without the use of another generator, because of the uncertainty of the setting for true zero beat. The frequencies ending in

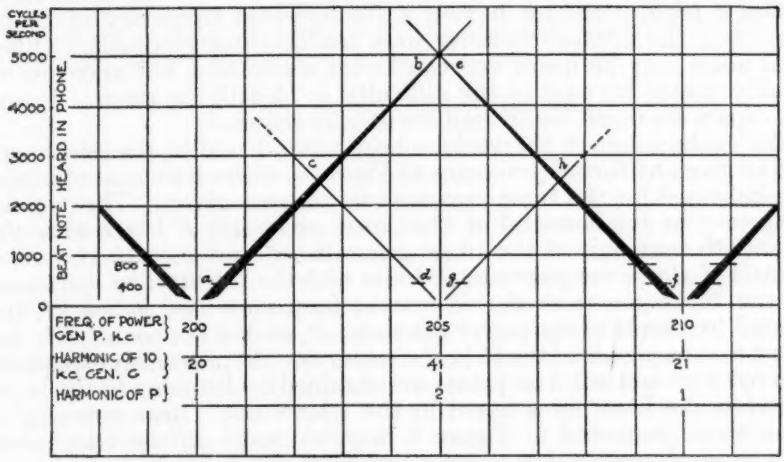

FIGURE 6.—*Chart used in explanation of the beat notes which are heard when working with the system described in the text*

2½, 5, and 7½ can be set accurately by matching beat notes in the telephone receivers, which are beats of beats, as described below.

Figure 6 illustrates how the various beat notes heard in the telephones can be interpreted; that is, whether the frequency to which the power generator P is set ends in zero or in some other number. The diagonal lines represent the beat notes heard in the telephones, and the breadth of the lines represents their relative strength. Thus it is seen that the beat notes occurring near the frequencies ending in zero are very loud or strong. Zero beat being indefinite, a setting is taken by matching with the note from a tuning fork, as described above. This method is simpler than providing an extra beat indicator to determine the desired frequency adjustment. When the frequency of the power generator P is increased from 200 kc, for example, as indicated in Figure 6, the beat note gradually gets higher and fainter, line *ab*, until at a frequency of the order of 204.5 kc the beat note is quite high, but a lower note, line *cd*, will also be heard, which becomes lower as the other becomes higher. Soon after the low note has become silent the high note will be heard to pulsate, and, with critical adjustment of the generator P beats with another beat note will be heard,

which permit a very accurate setting of the generator. This setting gives one of the 5 kc points, and is readily distinguished over a range of several hundred kilocycles by the aural method described. If the frequency of the power generator is increased further, the other high frequency beat note, line *ef*, becomes lower and stronger, and a weaker beat note, line *gh*, becomes higher and fainter. Further change in the power generator brings in a loud beat note and, finally, silence, or zero beat, in the telephones. This is another 10 kc point. The beat note represented at *b* is 5,000 cycles when a 10 kc fundamental is used. When the frequency of the power generator is being changed from *a* to *b* if conditions are right, another beat note may be heard at *c* and a precise setting made at this point, which will be midway between the 10 kc point and the 5 kc point. This setting is more difficult to obtain than the 5 kc point because it is indicated by the beats between two 2,500-cycle notes of very different intensities. When a piezo oscillator having a fundamental frequency of 25 kc was used, the 2,500-cycle notes were readily distinguishable. Other beat notes may be heard and can be set accurately, but may not be readily usable because of the difficulty in identifying them. Points 5 kc apart are much closer than are usually required.

An explanation of the various beat notes heard in the telephones can be given by further reference to Figure 6, where harmonic numbers are indicated for the three zero-beat frequencies given. The 200 kc frequency or fundamental of the power generator *P* beats with the twentieth harmonic of the 10 kc generator *G*, and the 210 kc fundamental of the power generator *P* beats with the twenty-first harmonic of the 10 kc generator *G*. When the frequency used is 205 kc, the second harmonic of the power generator *P*, or 410 kc, beats with the forty-first harmonic of the 10 kc generator *G*. As previously explained, the 202.5 kc and 207.5 kc points are obtained by listening to the beats between the beat notes heard in the telephones. Beat notes other than those indicated in Figure 6 may be heard in the telephones, but those described are usually sufficient for calibration purposes.

Although the 10 kc points can not be set precisely, they can be accurately determined by matching a beat note in the telephones with a corresponding note from the tuning fork. If the frequency of the fork is known it is only necessary to make the measurement on one side of zero beat.

3. MEASUREMENT OF AUDIO-FREQUENCY NOTE RESULTING FROM DIFFERENCE IN FREQUENCY BETWEEN PIEZO OSCILLATOR UNDER TEST AND GENERATOR

The determination of the difference in frequency between the piezo oscillator under test *P O* and generator *P* (fig. 3) is made by matching with a similar note from an audio-frequency generator. While this matching would seem to be an easy matter, sometimes in practice it is found to be very difficult, either because the note is weak or many harmonics are present, or it is modulated with some other frequency, such as 60 cycles, when the power supply line of this frequency is used to operate the tube of the piezo oscillator *P O*.

When the two notes are nearly matched, slow beats will be heard when listening in the two telephone receivers which are connected to the piezo oscillator *PO* and the audio-frequency generator *AF*, respectively. Beats may also be heard when there is a small

harmonic ratio between the frequencies. While it is convenient to have both notes coming from one headpiece when precise matching is desired, it is essential to be able to listen to each note separately during the process of adjustment, as, otherwise harmonics are very likely to be obtained.

4. MEASUREMENT OF AUDIO FREQUENCY WITH FREQUENCY METER

By means of the frequency meter *FM* (fig. 3) described in another section it is possible to check the results obtained with the audio-frequency generator *AF*. The check measurements involve two readings of the frequency meter *FM*, one when the generator *P* is adjusted to zero beat with the piezo oscillator *PO*, and the second when the generator *P* is adjusted in terms of the frequency standard *S*, by means of amplifier T, 10 kc generator *G*, and the special beat-indicator circuits as described above. The difference in the two readings of the frequency meter *FM* should give a result approximately the same as that obtained with the audio-frequency generator *AF*, and thus serves as a check on those measurements.

V. TEST PROCEDURE

In starting the test of a piezo oscillator, it is set up on a small portable table, and tried out using the type of tubes and voltages specified. A number of preliminary measurements are made as described below, including test for fundamental frequency, which is only a very approximate measurement, test to determine this frequency value within 1 or 2 kc, and test to discover any undesired frequencies. The apparatus used for these tests consists of the usual type of frequency meter and radio-frequency generator rather than the more complicated equipment described in this paper.

The fundamental frequency of the piezo oscillator is determined approximately by coupling a frequency meter to the oscillator and noting the setting at which the reading of the meter in the plate circuit of the piezo oscillator increases. If the coupling is too close, the piezo oscillator will stop oscillating, in which case the meter in the plate circuit will read the normal plate current of the tube. The coupling can readily be adjusted so that a momentary increase in the reading of the meter may be noted as the frequency meter passes through the fundamental frequency of the piezo oscillator In general, this coupling is such that no response will be obtained at a harmonic, and, therefore, the method may be relied upon to give the fundamental frequency within 1 or 2 per cent.

After the fundamental frequency has thus been determined roughly, a more precise determination is made, which may be of the order of 0.2 per cent This measurement is made by setting a small radio-frequency generator to zero beat with the piezo oscillator and measuring the frequency of the generator with a suitable frequency meter.

It is essential that a quartz plate which is to be used as a frequency standard have but one frequency at which it operates when circuit constants are not appreciably changed. One of the important tests upon a piezo oscillator, therefore, is that to determine whether the quartz plate may operate at a slightly different frequency than the one desired. Quartz plates are often found to have two or more frequencies separated a few hundred cycles. Such undesired fre-

quencies can often be found by setting a radio-frequency generator so that a certain audio-frequency note is produced in the telephone receivers in the piezo oscillator circuit. Changes are then made in the various adjustments of the piezo oscillator, and the quartz plate is turned from side to side. If the beat note suddenly changes to some other pitch, the quartz plate is operating at a different frequency, and will not be satisfactory as a standard. A gradual change in frequency is to be expected if, for example, the condenser setting of the piezo oscillator is varied. If the piezo oscillator appears to operate satisfactorily, it is wheeled into the room where the temperature is maintained constant 24 hours in the day. If the quartz plate requires grinding to bring it to the desired frequency, this work is done before the tests outlined above are made, and then the piezo oscillator is placed in the special room. The above tests complete the preliminary measurements.

The piezo oscillator remains in the constant-temperature room over night, and the first precision measurement of its frequency is made the following day. On the next day the precision measurements are repeated, and if the frequency measured is sufficiently close to the value of the previous day, the piezo oscillator is again tested for two frequencies or other peculiarities in operation, and if found to be satisfactory, is returned to the owner, and a test certificate prepared. However, if the measurements of the second day do not agree with those of the first day, the piezo oscillator is kept over and tried a third time, and efforts made to determine the cause of the disagreement in the measurements. Certificates are not issued for quartz plates which operate in an erratic manner.

If the piezo oscillator is to be tested at a given temperature, the temperature-controlled cabinet must be submitted with the piezo oscillator. The complete equipment is set up, and readings of the temperature near the quartz plate are noted at intervals until a constant temperature is obtained or until the limits within which the device operates are found. If the device is satisfactory in operation, the first precision frequency measurement may be made after the piezo oscillator has been at the required temperature at least 24 hours. The remainder of the test is conducted as has previously been described.

Figure 7 gives a view of the apparatus used in the constant-temperature room.

TABLE 1.—*Measurement of 1,370 kc piezo oscillator.*

[Values in kc]

Setting of generator *P*	Piezo oscillator under test	Generator *P* fundamental frequency	Frequency meter *FM*	Second harmonic	Audio generator *AF*
Zero beat with piezo oscillator under test	±1, 370	±685	685. 12	1, 370. 24	----------
Zero beat with standard	----------	685. 000	685. 00	1, 370. 00	0. 193
Frequency of piezo oscillator is 1,370.000+0.193=1,370.193 kc	----------	----------	----------	0. 24	----------

Table 1 shows data taken on a piezo oscillator for 1,370 kc. Reading from left to right, zero beat with the piezo oscillator at about 1,370 kc is taken by setting the generator *P* to half this frequency, or approximately 685 kc. Reading the frequency of the generator *P*

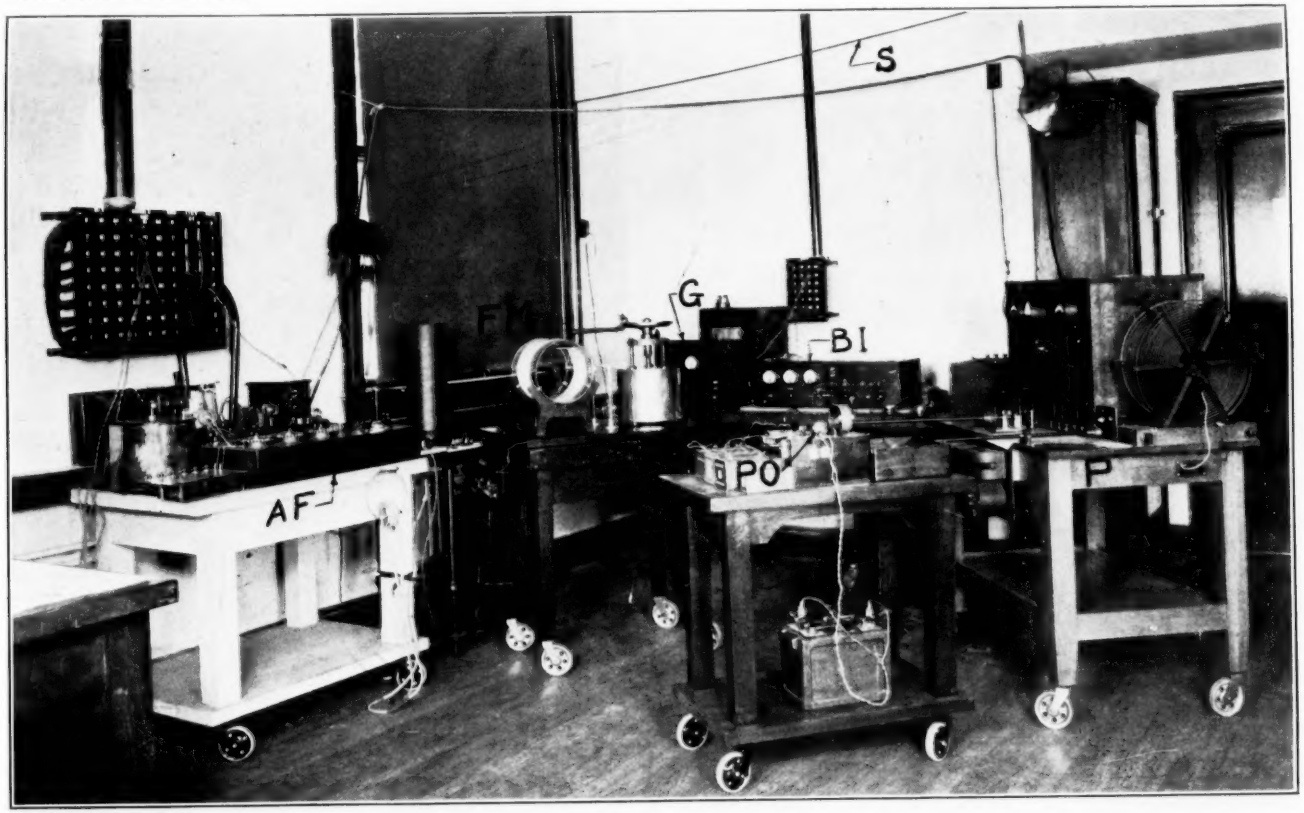

FIGURE 7.—*Apparatus used in testing piezo oscillators*

S, Wires leading from 200 kc standard; *G*, 10 kc generator; *BI*, special beat indicator; *P*, radio-frequency generator; *PO*, piezo oscillator under test; *FM*, frequency meter; *AF*, audio-frequency generator.

with the frequency meter *FM*, 685.12 kc is obtained, giving 1,370.24 kc for the fundamental frequency in terms of the frequency meter. In the second part of the measurement, zero beat is obtained with the standard, for which condition the generator *P* is set at 685.000 kc and the frequency meter *FM* indicates 685.00 kc, for which the second harmonic is 1,370.00 kc. The beat note between the piezo oscillator under test and the generator *P* is matched by comparison with the audio-frequency generator *AF* and a value of 0.193 kc obtained. It will be noticed that this value is in fair agreement with the difference obtained from the values in the "second harmonic" column. As the values in the latter column are twice the readings obtained from the frequency meter, the errors in the calibration of the latter are doubled. When this fact is considered, it will be apparent that the frequency-meter calibration was quite satisfactory. It will be noted that the frequency meter reading for zero beat with the piezo oscillator gave a higher frequency than for zero beat with the standard. The value, 0.193 kc, should, therefore, be added to 1,370.000 kc, giving 1,370.193 as the frequency of the piezo oscillator under test. The piezo oscillator probably will not hold its frequency to better than 0.01 per cent so that the value may be reported as 1,370.2 kc. The frequency meter readings are used only as a guide, or check, on the accuracy of the more precise measurements based on beat frequencies.

An interesting point may be noted here. In the above paragraph it is evident that the error in the frequency meter calibration is multiplied or increased when the frequency used in the test is a fractional value of the fundamental of the piezo oscillator. Conversely the error in the frequency meter calibration is divided or reduced when the frequency used in the test is a harmonic of the fundamental of the piezo oscillator. If an attempt is made to gain this advantage of the reduction in the error of the frequency meter measurement in the case of broadcast frequency testing, other difficulties may more than offset it. It may, however, be applied with considerable success in the measurement of the frequency of quartz plates having a low frequency fundamental, and the possible error in the frequency meter calibration may be reduced to a small amount.

If the frequency of the piezo oscillator is within 50 or 100 cycles of being correct, it is convenient to change the second step in the measurement so that the generator *P* is set off the desired frequency by a known amount, which can be readily accomplished by matching the beat note in the standard circuits with the note from a tuning fork. Table 2 shows results obtained in such a test.

TABLE 2.—*Measurement of 940 kc piezo oscillator*

[Values in kc]

Setting of generator *P*	Piezo oscillator under test	Generator *P* fundamental frequency	Frequency meter *FM*	Second harmonic	Audio generator *AF*
Zero beat with piezo oscillator under test	±940	±470	469.99	939.98	
Generator *P* set off from standard using tuning fork		470.000−0.400=469.000	469.55	939.10	0.833
Frequency of piezo oscillator is 469.6×2+0.833=940.033 kc				0.88	

The first part of the measurement is made in a similar manner to that given for Table 1. In the second part of the measurement if

zero beat is obtained with the standard as in Table 1, the beat note with the piezo oscillator would be too low to hear. The generator *P* is therefore set off from zero beat by matching the note between the generator *P* and the standard with a 400-cycle tuning fork, which gives 469.600 kc as the generator frequency. According to the frequency meter *FM*, it is set at 469.55 kc with a second harmonic of 939.10 kc. The beat note between the generator *P* and the piezo oscillator *PO* is matched with a corresponding note from the audio-frequency generator *AF* which gives a reading of 0.833 kc. It will be noted that the difference in the two frequency meter readings gives 0.88 kc, which indicates that no error from harmonics has been introduced. The frequency of the piezo oscillator *PO* is therefore measured as 940.033 kc, which will be reported as 940.0 kc.

VI. CONCLUSION

While the method of test described has had reference to the testing of piezo oscillators, the system is likewise applicable to the measurement of the frequency of a transmitting station, or the calibration of a frequency meter. The latter application of the system has been described in the author's paper mentioned on page 118. In the case of the measurement of the frequency of a radio station, the piezo oscillator under test above would be replaced by a radio receiving set tuned to the station whose frequency is to be measured.

The method described is a precise method, and its precision can be increased further by the use of an oscillograph. It is capable of adequate accuracy for any apparatus to be tested.

The system has the following advantages: (1) great accuracy, (2) high precision, (3) use of a given standard over a wide range, (4) large number of calibration points available, (5) flexibility of system, and (6) ease of operation.

1. Great accuracy is possible with the system and method used because all measurements are based upon a temperature-controlled piezo oscillator, and the final frequency value is in terms of the standard and an audio-frequency generator which holds its calibration over long periods without appreciable change.

2. High precision is obtained in the measurements because of the fact that beat notes are used in making the various adjustments.

3. The usefulness of a given piezo oscillator used as the standard may be greatly extended by reason of the many harmonics which are available from the system as a whole.

4. The many calibration points available come from the harmonics spaced 5 kc apart and the use of tuning-fork notes to displace the setting an accurately known amount.

5. The method is flexible in that it can be adapted to many kinds of frequency measurements, including those on piezo oscillators, radio stations, and frequency meters.

6. The system is quite simple to operate when the accuracy and large number of points obtainable are considered.

In conclusion, by means of the method and apparatus described, results of high accuracy are obtained in relatively short time in the testing of piezo oscillators for broadcasting stations.

WASHINGTON, August 15, 1929

PHASE EQUILIBRIA IN THE SYSTEM SiO_2–ZnO

By E. N. Bunting

ABSTRACT

A study of phase equilibria in the condensed system SiO_2-ZnO by the quenching method shows the existence of (*a*) only one compound, Zn_2SiO_4, the melting point of which is 1,512° C.; (*b*) a region of two immiscible liquid phases in equilibrium with cristobalite at 1,695° C., extending from 2 to 35 mol per cent ZnO; (*c*) a eutectic between tridymite and Zn_2SiO_4 at 1,432° C. and 49.1 mol per cent ZnO; and (*d*) a eutetic between ZnO and Zn_2SiO_4 at 1,507° C. and 77. 5 mol per cent ZnO. The melting point of ZnO is found to be 1,975° ± 25° C.

An iridium vessel is described which can be used in an induction furnace to obtain constant temperatures up to 2,300° C. in an oxidizing atmosphere.

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I. INTRODUCTION

Since the available data on phase equilibria in the SiO_2-ZnO system were very incomplete and contradictory, a rather complete study of this system has been made as a preliminary to an investigation of the ternary system SiO_2-ZnO-Al_2O_3.

The existence of a zinc metasilicate, $ZnSiO_3$, has been reported by several investigators.[1] Gorgeu,[2] however, could not obtain the metasilicate from melts of $ZnO + SiO_2$ with Na_2SO_4, only the orthosilicate being formed.

The orthosilicate, Zn_2SiO_4, is found as the mineral willemite. Stein gives the melting point of the synthetic compound as 1,484° C. and Jäger and van Klooster give 1,509° C.

II. GENERAL METHOD

Because of the low velocity of crystallization of molten silicate mixtures it was necessary to use the quenching method to study the equilibrium conditions. A small sample (10 to 20 mg) of the mixture under investigation was inclosed in a platinum capsule and

[1] Stein, Zeit. anorg. Chem., **55**, p. 159; 1907. van Klooster, Zeit. anorg. Chem., **69**, p. 142; 1910. Jäger and van Klooster, Proc. Royal Acad. Sci. Amst., **18**, p. 896; 1916. Ebelmen, Ann. de Chim. Phys. (3), **33**, p. 34; 1851. Schulze and Stelzner, Neues Jahrb. Min., **1**, p. 150; 1881. Traube, Berichte, **26**, p. 2735; 1893. Mulert, Zeit. anorg. Chem., **75**, p. 220; 1912. Rüger, Keram. Rundschau, **31**, p. 100; 1923.

[2] Gorgeu, Comp. rend., **104**, p. 120; 1887.

held at a constant temperature until equilibrium was attained between the phases present. It was then rapidly cooled by dropping into water or mercury, so that no change in the equilibrium could occur, and the material examined under the petrographic microscope to identify the phases present.

Figure 1 shows the resistance furnace used. It was 40 cm long and the heating unit consisted of 13.7 m of wire,[3] 0.81 mm in diameter,

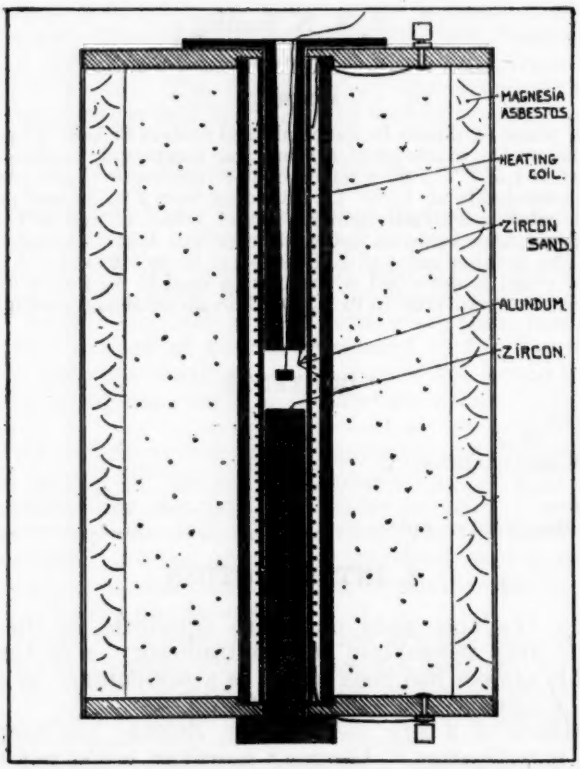

FIGURE 1.—*Diagram of Pt–Rh resistance furnace used in quenching experiments*

made from an alloy containing 60 per cent Pt and 40 per cent Rh. About 1 kw was required to hold it at 1,700° C. The platinum capsule was suspended in the furnace chamber by means of a fine platinum wire attached to a larger platinum wire. After equilibrium was attained the bottom plug was removed and the capsule dropped into water by pulling it up until its small supporting wire broke. Temperatures in the furnace were held constant with a modified thermostat of the type developed at the Geophysical Laboratory,[4] and were measured with a disappearing filament optical pyrometer sighted through the conical opening in the upper plug of the furnace. A calibrated Pt-PtRh thermocouple [5] placed in the center of the furnace

[3] The wire was fabricated by the chemical metallurgy section of this bureau. Recently pure rhodium wire has been used as the heating unit.
[4] Roberts, J. Opt. Soc. Am. and Rev. Sci. Inst., **11**, p. 171; 1925.
[5] The optical pyrometer and thermocouple were calibrated by the pyrometry section of this bureau.

chamber checked the temperature readings obtained with the optical pyrometer to within 2° C. at 1,400° C., both pyrometer and thermocouple being certified to ± 5° C. at this temperature. At the higher temperatures up to 1,700° C. the pyrometer was certified to ± 10° C.

III. THE SiO_2–ZnO MIXTURES

The SiO_2-ZnO mixtures investigated were prepared from selected rock crystal (99.7 per cent SiO_2 after grinding to 200 mesh) and zinc oxide specially prepared by the New Jersey Zinc Co. and containing not more than 0.10 per cent total impurities.[6] The mixtures were prepared in stick form and prefused in the oxyhydrogen flame. The fused material was pulverized in a steel mortar and ground in an agate mortar. Three fusions and grindings were made to insure a homogeneous mixture.[7] All mixtures were found to contain one to two-tenths of a per cent of Fe_2O_3, introduced in the pulverizing process. The mixtures were all held at the furnace temperatures for one-half hour or more before quenching.

IV. RESULTS

The data obtained are given in the table and in Figure 2.

Results with SiO_2-ZnO mixtures

Composition, mol per cent ZnO	Furnace temperature	Phases present	Composition, mol per cent ZnO	Furnace temperature	Phases present
	°C.			°C.	
1.8	1,700	One glass.	58.5	1,490	All glass.
3.1	1,695	2 glasses+cristobalite.		1,480	Glass+Zn_2SiO_4.
19.7	1,695	Do.	60.4	1,505	All glass.
27.0	1,695	Do.		1,500	Glass+Zn_2SiO_4.
31.2	1,695	Do.	65.0	1,515	All glass.
34.3	1,695	Do.		1,510	Glass+Zn_2SiO_4.
37.4	1,610	All glass.	66.7	1,515	All glass.
	1,600	Glass+cristobalite.		1,510	Zn_2SiO_4.
43.3	1,530	All glass.	69.4	1,515	All glass.
	1,520	Glass+cristobalite.		1,510	Glass+Zn_2SiO_4.
44.5	1,510	All glass.	71.9	1,515	All glass.
	1,500	Glass+cristobalite.		1,510	Glass+Zn_2SiO_4.
46.2	1,490	All glass.	73.9	1,510	All glass
	1,480	Glass+cristobalite.		1,505	Glass+Zn_2SiO_4.
47.0	1,470	All glass.	75.2	1,510	All glass.
	1,465	Glass+tridymite.		1,505	Glass+Zn_2SiO_4.
48.3	1,465	All glass.	76.5	1,510	All glass.
	1,455	Glass+tridymite.		1,505	Glass+Zn_2SiO_4.
49.1	1,435	All glass.	78.0	1,540	All glass.
	1,430	Tridymite+Zn_2SiO_4.		1,535	Glass+ZnO.
51.0	1,440	All glass.	79.5	1,570	All glass.
	1,435	Glass+Zn_2SiO_4.		1,560	Glass+ZnO.
51.6	1,450	All glass.	81.0	1,590	All glass.
	1,445	Glass+Zn_2SiO_4.		1,580	Glass+ZnO.
52.5	1,455	All glass.	82.9	1,610	All glass.
	1,450	Glass+Zn_2SiO_4.		1,600	Glass+ZnO.
54.3	1,460	All glass.			
	1,455	Glass+Zn_2SiO_4.			

[6] Analysis furnished by the New Jersey Zinc Co.
[7] All mixtures were analyzed by J. A. Scherrer of the analytical section of the chemistry division of this bureau.

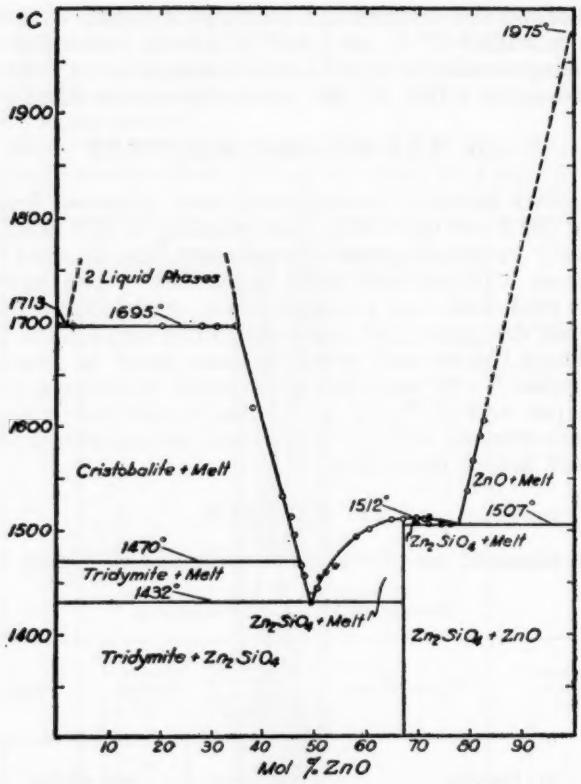

FIGURE 2.—*Phase diagram for the system SiO_2–ZnO*

V. DISCUSSION

These experiments show that only one compound—Zn_2SiO_4, zinc orthosilicate—is formed at high temperatures. Its melting point is 1,512° C ± 3° C. It forms a eutectic with tridymite at 1,432° C. and 49.1 per cent ZnO, and a eutectic with ZnO at 1,507° C. and 77.5 mol per cent ZnO. The optical properties of the Zn_2SiO_4 prepared agree closely with those of the natural mineral, willemite,[8] and are as follows:[9] Uniaxial positive (tetragonal or hexagonal) occurring as irregular grains with no characteristic crystal form or habit and with no good cleavage. Indices of refraction for sodium light are $\omega = 1.692$, $\epsilon = 1.720$, both ± 0.003. Near the eutectic composition with tridymite the Zn_2SiO_4 occurs as fine fibrous crystals, often as spherulitic radiating aggregates.

No evidence of the existence of the metasilicate was found. Examination at high magnification (1,000×) of the fully crystallized mixtures containing 49.1 and 51.0 mol per cent of ZnO held at 1,350°, 1,300°, 1,200°, and 1,100° C., respectively, for 70 hours each, showed them to contain only tridymite (25 to 30 per cent) and zinc ortho-

[8] Am. Mineral, **10**, p. 187; 1927.
[9] H. Insley, of this bureau, determined the optical properties and collaborated in the petrographic examination of some of the mixtures.

silicate.[10] At a magnification of 100 to 200×, the material appears to be homogeneous and might easily be mistaken for a metasilicate. These same mixtures were also fused with sodium tungstate at 1,000° for 72 hours and the melt extracted with warm water and dilute ammonia solution. Only zinc orthosilicate was found in the residue. X-ray spectrograms [11] of the mixtures, containing 51.6 mol per cent ZnO, quenched at 1,440° C., and 65.0 mol per cent ZnO, quenched at 1,505° C., showed identical patterns, proving the absence of a metasilicate in the region of 50 mol per cent ZnO. X-ray spectrograms of the 48.3 mol per cent ZnO and 51.6 mol per cent ZnO mixtures held at 1,350° C. for two hours and containing tridymite with zinc orthosilicate were also identical.

The two liquid phases occurring at 1,695° and between 2 to 35 mol per cent ZnO were first noted by J. W. Greig.[12] The upper boundary of this region was not investigated, as it is above the temperature attainable in the resistance furnace. The Ir-Pt alloy furnace described below (fig. 3) could not be used for this purpose, as vaporization from the hole at high temperatures could not be prevented, and the mixture in the hole did not remain of uniform composition.

The melting point of cristobalite given as 1,713° C., in figure 2, is taken from the data published by J. W. Greig.[13]

VI. THE MELTING POINT OF ZnO

The only datum given in the literature on the melting point of ZnO is that it is above 1,800° C.[14] As this is above the temperature obtainable in a platinum resistance furnace, it was necessary to design a furnace which could be operated at high temperatures in an oxidizing atmosphere in order to prevent the reduction of the ZnO. Iridium, with a melting point of 2,300° C., is a suitable heating element, since it does not oxidize when heated rapidly to temperatures above 1,200° C.[15] Instead of pure iridium, an alloy with 27 per cent platinum, melting at 2,150° C., was employed in the form of a button which was formed by melting mixed Ir-Pt sponge in the bottom of a thoria crucible.[16] (See fig. 3.) When this crucible was surrounded with an insulating layer of powdered thoria one-half inch thick, contained in an alundum thimble, the button within could be heated up to its melting point when placed in the high-frequency field of an Ajax induction furnace. By adjusting the spark gap every minute or two the temperature of the button could be held constant

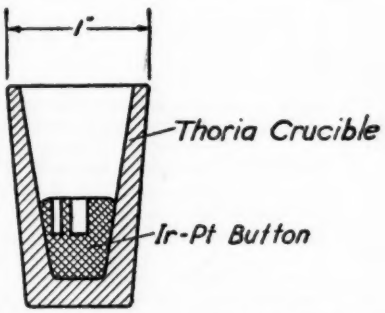

FIGURE 3.—*Crucible with iridium vessel used to obtain temperatures up to 2,300° C. in an oxidizing atmosphere*

[10] See footnote 9.
[11] X-ray spectrograms were made by E. C. Groesbeck, of the metallurgical division of this bureau.
[12] Greig, Am. J. Sci., **13**, p. 137; 1927.
[13] Greig, Am. J. Sci., **13**, p. 10; 1927.
[14] Libman. J. Am. Ceram. Soc., **5**, p. 488; 1922.
[15] The dissociation temperature of IrO_2. See Becker, Diss. Darmstadt; 1927.
[16] This crucible and Ir button were fabricated by the chemical metallurgy section of this bureau.

within ±10° C. Temperatures were measured with an optical pyrometer sighted on the outer small hole, both holes giving the same reading when empty.

A small piece of ZnO, which had previously been fused in the oxygen carbon arc, was placed in the center hole of the button and heated. Above 1,950° C. complete evaporation of the charge occurred within a few seconds. However, when a layer of Ir–Pt sponge (of the same composition as the button) was tamped in above the powdered ZnO, a fused pellet of ZnO was obtained on heating to 1,975° for a few seconds. A repetition of this procedure at 1,960° did not fuse the ZnO, while at 1,985° a fused pellet was also obtained. The optical pyrometer was used immediately after calibration and was certified to ±25° C. at this temperature.

The author is indebted to E. W. Washburn, of this bureau, under whose general supervision the work was done.

WASHINGTON, September 4, 1929.

EFFECT OF SMALL CHANGES IN TEMPERATURE ON THE PROPERTIES OF BODIES

By Mayo D. Hersey

ABSTRACT

When it is found necessary to determine the effect of small departures from normal temperature upon some property of a body or system of bodies, such as the stiffness of a steel spring, the vibration frequency of a tuning fork, or the accuracy of an instrument, it is usually done either (*a*) by a detailed computation or (*b*) by a direct experiment in which the temperature is actually varied.

After reviewing and illustrating the usual methods of solution a general mathematical treatment of the problem is given, from which two additional methods are derived that can sometimes be usefully applied: (*a*) A simple calculation, made possible by the theory of dimensions, which does not require any detailed formula for the property in question; and (*b*) a combined theoretical and experimental solution, in which the experimental factors have been reduced to a minimum and can be determined without varying the temperature of the body itself, provided the thermal properties of the component materials are known.

Finally, it is pointed out that the same treatment can be extended to any other condition analogous to temperature, such as hydrostatic pressure.[1]

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[1] Recent investigations in which it was found necessary to compute the effect of changes in temperature and in pressure on the properties of bodies have been published by E. A. Harrington, J. Opt. Soc. Am., **18**, pp. 89 to 95; 1929; and by P. W. Bridgman, Proc. Am. Acad. Arts. Sci., **63**, pp. 401 to 420; 1929.

I. INTRODUCTION

In physical and engineering investigations involving the properties of bodies (as distinguished from substances or materials) it is often necessary to know at least approximately what will be the effect of small departures from the normal working temperature. If the magnitude of the property in question is represented by P, the effect of any small change in temperature, Δt, can obviously be obtained from the relation

$$\frac{\Delta P}{P}=\left(\frac{1}{P}\frac{dP}{dt}\right)\Delta t \tag{1}$$

provided the value of the temperature coefficient $(1/P)(dP/dt)$ is known.

The quantity P may represent, for example, some familiar physical property of a single homogeneous body or some performance characteristic of an instrument or machine. The magnitude of the temperature coefficient $(1/P)(dP/dt)$ must obviously depend upon various different factors, including the physical properties of the component materials.

The general problem considered in this paper is that of determining the value of the temperature coefficient $(1/P)(dP/dt)$ or, in other words, the value of the fractional or relative rate of change of the property in question with respect to temperature.

The usual practice is to compute the temperature coefficient from a detailed formula for the property P if such a formula can be written, otherwise to have recourse to a direct experiment in which the values of P are observed at different temperatures. In this paper two additional methods of solution are described after first reviewing and illustrating the more usual methods.

II. EXAMPLES ILLUSTRATING THE USUAL METHODS OF SOLUTION

The usual methods of solution, particularly the computation method, can readily be illustrated by three simple examples taken from the field of elasticity, the first involving pure bending, the second pure twisting, and the third involving complex stresses.

These examples will at the same time serve to illustrate the use of logarithmic differentiation and the use of the dot above any quantity to denote the fractional or relative rate of change of that quantity with respect to temperature (1, 2).[2] [3] For convenience both short cuts will be employed throughout the paper. This present use of the dot to indicate logarithmic differentiation with respect to temperature need not be confused with its use to represent ordinary differentiation with respect to time in mechanics. The logarithmic derivative of any quantity Q with respect to t is defined by the expression $d \log Q/dt$ and therefore is equal to $(1/Q)(dQ/dt)$ and will be denoted simply by $\dot{Q}$.

[2] Figures in parentheses here and throughout the text refer to the numbers under "References" at the end of this paper.

[3] Previously used with advantage in papers on The Theory of the Stiffness of Elastic Systems, and Vibration Frequencies of Elastic Systems (1, 2).

1. STIFFNESS OF A FLAT SPRING OF UNIFORM CROSS SECTION

Let the length, breadth, and depth (or thickness) of the spring be denoted by L, B, and D, respectively. Consider the spring fixed at one end like a cantilever beam and loaded at the other end by the application of a force F. Let Y denote the deflection of the spring at the extreme end due to the force F. The spring stiffness S may be defined by the expression F/Y and corresponds, in this example, to the general property P, whose temperature coefficient is desired.

Under the foregoing conditions the usual formula for the deflection of a cantilever beam leads to the relation

$$S=\frac{BED^3}{4L^3} \tag{2}$$

in which E is Young's modulus of elasticity. Differentiating logarithmically to obtain the effect of temperature change,

$$\frac{1}{S}\frac{dS}{dt}=\frac{1}{B}\frac{dB}{dt}+\frac{1}{E}\frac{dE}{dt}+\frac{3}{D}\frac{dD}{dt}-\frac{3}{L}\frac{dL}{dt} \tag{3}$$

or more simply

$$\dot{S}=\dot{B}+\dot{E}+3\dot{D}-3\dot{L} \tag{4}$$

If the material of the spring can be treated as homogeneous and isotropic, so that the body expands uniformly in all directions without distortion, $\dot{B}=\dot{D}=\dot{L}$ and equation (4) become

$$\dot{S}=\dot{L}+\dot{E} \tag{5}$$

This result amounts to the statement that the temperature coefficient of the stiffness of the spring is equal to the linear thermal expansivity of the material plus the temperature coefficient of Young's modulus. For the usual materials, $\dot{L}$ is intrinsically positive while $\dot{E}$ is intrinsically negative.

2. TORSIONAL STIFFNESS OF A WIRE OF CIRCULAR CROSS SECTION

Let M denote the torque or moment needed for maintaining an angular deflection θ at the free end of a vertical wire of length L and diameter D. From the theory of elasticity, if the material is isotropic and homogeneous,

$$M=\frac{\pi D^4\mu}{32L}\cdot\theta \tag{6}$$

in which μ denotes the shear modulus of elasticity. Defining the torsional stiffness T by the ratio M/θ, that is, torque per unit twist, equation (6) gives

$$T=\frac{\pi D^4\mu}{32L} \tag{7}$$

Differentiating logarithmically with respect to the temperature and making use of the fact that $\dot{D}=\dot{L}$, we obtain

$$\dot{T}=3\dot{L}+\dot{\mu} \tag{8}$$

again a linear function of the thermal expansivity and the temperature coefficient of one of the elastic moduli, this time the temperature coefficient of the shear modulus.

3. VIBRATION FREQUENCY OF A FLAT CIRCULAR DIAPHRAGM, CLAMPED AT THE EDGE

Let n denote the frequency of the slowest vibration of a diaphragm of thickness L and diameter D, composed of an isotropic, homogeneous, perfectly elastic material of density ρ, Young's modulus E and Poisson's ratio σ. According to Rayleigh (3) [4] after converting into the above notation and working out an approximate value of the numerical factor

$$n=\frac{1.88}{\sqrt{1-\sigma^2}}\left(\frac{L}{D^2}\right)\sqrt{\frac{E}{\rho}} \tag{9}$$

Differentiating as before, and making use of the identity $d\sigma/dt=\sigma\dot{\sigma}$, we find that

$$\dot{n}=\left(\frac{\sigma^2}{1-\sigma^2}\right)\dot{\sigma}+\dot{L}-2\dot{D}+\frac{\dot{E}}{2}-\frac{\dot{\rho}}{2} \tag{10}$$

Since, however, $\dot{D}=\dot{L}$ and $\dot{\rho}=-3\dot{L}$ for isotropic materials, equation (10) can be written

$$\dot{n}=\left(\frac{\sigma^2}{1-\sigma^2}\right)\dot{\sigma}+\frac{\dot{L}}{2}+\frac{\dot{E}}{2} \tag{11}$$

This gives the result as a linear function of three of the temperature coefficients of the material, one of which, the temperature coefficient of Poisson's ratio, can be replaced by other data that are more readily available.

Thus from the theory of elasticity, for the type of material under consideration, the three elastic constants E, μ, and σ are connected by a definite relation,

$$\sigma=\frac{1}{2}\frac{E}{\mu}-1 \tag{12}$$

from which it is evident that it should be possible to express $\dot{\sigma}$ in terms of $\dot{E}$ and $\dot{\mu}$. Differentiating, we obtain

$$\dot{\sigma}=\left(\frac{1+\sigma}{\sigma}\right)(\dot{E}-\dot{\mu}) \tag{13}$$

Accordingly equation (11) reduces to

$$\dot{n}=\frac{\dot{L}}{2}+\frac{1}{2}\left(\frac{1+\sigma}{1-\sigma}\right)\dot{E}-\left(\frac{\sigma}{1-\sigma}\right)\dot{\mu} \tag{14}$$

a linear function of the thermal expansivity, temperature cofficient of Young's modulus, and temperature coefficient of the shear modulus.

[4] An alternative formula involving total mass in place of density is given in (2), footnote 3, p. 444.

Taking Poisson's ratio = 3/10 as a rough approximation gives for equation (14)

$$\dot{n}=\frac{\dot{L}}{2}+\frac{13}{14}\dot{E}-\frac{3}{7}\dot{\mu} \tag{15}$$

from which the approximate magnitude of $\dot{n}$ can readily be computed for various materials upon consulting tables of published experimental data for the appropriate values of $\dot{L}$, $\dot{E}$, and $\dot{\mu}$.

4. EXPERIMENTAL SOLUTION

To determine the temperature coefficient of any property P when the detailed formula for this property as exemplified by equations (2), (7), or (9) is not available, the most obvious and usual procedure is to set up the apparatus in question and make tests in which the temperature is actually varied. The temperature must be appropriately controlled, allowing time for thermal equilibrium to be reached. Preferably observations of P should be taken both above and below the normal working temperature at which the value of $\dot{P}$ is required. A sufficient range of temperature should be covered so that in plotting P against t the slope can be determined graphically with the requisite precision. Dividing the slope (in proper units) at any given temperature by the value of P at that temperature gives the corresponding value of the temperature coefficient $\dot{P}$.

The observations may be extended, if desired, over a sufficient range of temperature to permit plotting $\dot{P}$ as a function of temperature. This type of experiment, however, can not do more than provide discrete numerical values of $\dot{P}$ applicable to the identical apparatus under test. It does not throw any light on the functional relationship between $\dot{P}$ and the temperature coefficients of the component materials, $\dot{L}$, $\dot{E}$, $\dot{\mu}$, etc., as illustrated by equations (5), (8), or (14). Also it requires a specialized laboratory technique in order to work with actual changes of temperature.

III. GENERAL MATHEMATICAL THEORY

From a consideration of the nature of the variables entering the problem it will readily become apparent why the solution in every case takes the form of a linear function of the thermal expansivity and other thermal properties [5] of the component materials.

The character of a body or system of bodies depends evidently upon its size and shape and upon the properties of the component materials. If the system is homogeneous and isotropic, it can be defined by some linear magnitude L, together with as many length ratios $r_1 \ldots r_l$ as may be needed to fix the geometrical shape of the system, and the appropriate properties of materials, $p_1 \ldots p_m$.

When the system is not homogeneous and isotropic, the distribution of the values of each one of the p's must be indicated. This can most readily be done by selecting one point, and, if necessary, one plane and one stated direction at that point, where the absolute magnitude of the property will be given, and then expressing the distribution of the property by ratios of other values to this one.

[5] For brevity, the term "thermal properties" will be used collectively to denote the temperature coefficients of the properties of the materials, together with their thermal expansivities.

When two bodies of unequal absolute size possess the same distribution of length ratios, they are said to be geometrically similar or to have the same geometrical shape. By analogy, two bodies or systems of bodies may be said to have the same generalized shape when they possess the same relative distribution of properties (1).[6]

A system which is not homogeneous and isotropic can, therefore, be completely identified or described by giving its linear magnitude L and the magnitudes of the properties $p_1 \cdots p_m$, together with all ratios of like quantities, $r_1 \cdots r_l$, including both ratios of linear magnitudes and ratios of properties of materials, that may be needed to specify the generalized shape.

The property P may depend not only on the intrinsic character of the system as defined by L, $r_1 \cdots r_l$, and $p_1 \cdots p_m$, which may be termed internal variables, but also on a number of other quantities, $q_1 \ldots q_n$, which might be termed the external variables, and which, in general, are independent of temperature. Thus the entire list of independent variables governing the magnitude of P can be divided into the four groups or classes mentioned above and we may write

$$P=f(L, r_1 \ldots r_l, p_1 \ldots p_m, q_1 \ldots q_n) \tag{16}$$

where the form of the function f may or may not be known.

As a step toward investigating the effect of temperature on the property P in the light of equation (16) let us consider any system of N physical quantities Q_o, $Q_1, \cdots Q_{N-1}$ which are definitely related, so that

$$Q_o=f(Q_1, \cdots Q_{N-1}) \tag{17}$$

By ordinary differentiation

$$dQ_o=\left(\frac{\partial Q_o}{\partial Q_1}\right)dQ_1+\cdots \tag{18}$$

Hence by logarithmic differentiation

$$\frac{dQ_o}{Q_o}=\left(\frac{\partial Q_o/Q_o}{\partial Q_1/Q_1}\right)\frac{dQ_1}{Q_1}+\cdots=\left(\frac{\partial \log Q_o}{\partial \log Q_1}\right)\frac{dQ_1}{Q_1}+\cdots \tag{19}$$

or

$$\dot{Q}_o=\left(\frac{\partial \log Q_o}{\partial \log Q_1}\right)\dot{Q}_1+\cdots \tag{20}$$

The same computation can now be applied to equation (16), taking P as the equivalent of Q_o, and the quantities L, $r_1 \cdots r_l$, $p_1 \cdots p_m$, $q_1 \cdots q_n$ as equivalent to $Q_1 \cdots Q_{N-1}$. Since in general $q_1 \cdots q_n$ are wholly unaffected by temperature, we obtain

$$\dot{P}=\left(\frac{\partial \log P}{\partial \log L}\right)\dot{L}+\left(\frac{\partial \log P}{\partial \log r_1}\right)\dot{r}_1+\cdots+\left(\frac{\partial \log P}{\partial \log p_1}\right)\dot{p}_1+\ldots+\left(\frac{\partial \log P}{\partial \log p_m}\right)\dot{p}_m \tag{21}$$

From equation (21) it is clear that $\dot{P}$ must be a linear function of the thermal properties $\dot{L}$, $\dot{r}_1 \cdots \dot{r}_l$, $\dot{p}_1 \cdots \dot{p}_m$ in all cases, regardless of the form of the function f.

[6] See p. 571 for rolled sheet metal as an illustration of bodies having the same generalized shape, and for further discussion of this concept. Two pendulums of different sizes having variable densities similarly distributed constitute another such example.

When the generalized shape can be treated as sensibly constant, $\dot{r}_1 \ldots \dot{r}_l$ may be set equal to zero, and then equation (21) reduces to

$$\dot{P}=\left(\frac{\partial \log P}{\partial \log L}\right)\dot{L}+\left(\frac{\partial \log P}{\partial \log p_1}\right)\dot{p}_1+\cdots\left(\frac{\partial \log P}{\partial \log p_m}\right)\dot{p}_m \qquad (22)$$

or more simply

$$\dot{P}=C_o\dot{L}+C_1\dot{p}_1+\cdots+C_m\dot{p}_m \qquad (23)$$

in which C_o, $C_1, \cdots C_m$ denote the dimensionless, isothermal coefficients $(\partial \log P/\partial \log L)$, $(\partial \log P/\partial \log p_1)$, etc.

The restriction of equation (23) to a constant generalized shape is not a prohibitive one because (a) for homogeneous and isotropic bodies the generalized shape is the same as the geometrical shape and is actually constant; (b) for many bodies that are not homogeneous and isotropic the variation of $r_1 \cdots r_l$ with temperature is a second-order effect which can be neglected; and (c) when not negligible, as, for example, in considering the efficiency of a machine built of cast iron having its bearings fitted with brass bushings, the effect of temperature on the ratios $r_1 \cdots r_l$ can sometimes be calculated in detail by conventional methods and superposed on the solution obtained for a system of constant generalized shape.

From equation (23) it is evident that a complete experimental solution can be obtained without varying the temperature, if appropriate experiments are made for evaluating the isothermal coefficients $C_o, C_1, \cdots C_m$, and provided the thermal properties of the component materials are already known. These are usually available in published tables to a sufficient degree of approximation for the purpose in hand; if not, they can be determined by testing the component materials as such, without reference to the particular form of the bodies in question.

In actual practice the procedure suggested by equation (23) can be further simplified, as will be shown by means of the theory of dimensions.

IV. DIMENSIONAL THEORY

A number of very interesting conclusions can be deduced from equation (17) if it is understood in what follows that this equation expresses a qualitatively complete relation. If it is incomplete—that is, if any essential quantity has been overlooked in making up the list of independent variables $Q_1 \cdots Q_{N-1}$ on which the value of Q_o depends—we should not be warranted in applying the following analysis. If, however, the equation is overcomplete—that is, contains one or more quantities that are superfluous—no harm will be done and the extra variables introduced will automatically drop out again later.

For convenience equation (17) will further be restricted to systems of constant generalized shape or to different systems of the same generalized shape, so that the ratios $r_1 \cdots r_l$ need not be explicitly mentioned, and therefore the variables Q_o, $Q_1 \cdots Q_{N-1}$ represent N different kinds of physical quantities.

It is also understood that the form of the function f is entirely unknown, for if it were already known we should have nothing to gain by further inquiry and could proceed at once to the usual solution by differentiation illustrated by three examples earlier in the paper.

It follows from Buckingham's Π-theorem (4, 5) that equation (17) must be reducible to the form (7)

$$\Pi_o = \phi\ (\Pi_1,\ \Pi_2,\ \cdots\ \Pi_j) \tag{24}$$

in which the function ϕ is unknown, but in which the Π's are known and represent all of the independent dimensionless products that can be formed from the N physical quantities involved, and in which $j = N-k-1$, where k is the number of fundamental units (6) needed for measuring the N quantities.

In equation (24) Π_o represents the dimensionless product containing Q_o, together with as many of the quantities $Q_1 \cdots Q_k$ as may be found necessary to cancel out the dimensions of Q_o; that is,

$$\Pi_o = (Q_1^{\alpha_o} Q_2^{\beta_o} \cdots Q_k^{\kappa_o})\ Q_o \tag{25}$$

in which the exponents $\alpha_o, \beta_o, \cdots \kappa_o$ are pure numbers, some of which may be zero in any concrete example. In like manner we can write for any one of the products $\Pi_1 \cdots \Pi_j$ serving as arguments of the unknown function ϕ,

$$\Pi = (Q_1^{\alpha} Q_2^{\beta} \cdots Q_k^{\kappa})\, Q \tag{26}$$

Substituting from equation (25) into equation (24) and solving for Q_o gives finally

$$Q_o = Q_1^{-\alpha_o} Q_2^{-\beta_o} \cdots Q_k^{-\kappa_o} \phi(\Pi_1,\ \Pi_2,\ \cdots\ \Pi_j) \tag{27}$$

Upon identifying the general quantities $Q_o, Q_1, \cdots Q_{N-1}$ of equation (27) with the classified quantities P, L, $p_1 \cdots p_m$ and $q_1 \cdots q_n$ of equation (16), and omitting $r_1 \cdots r_t$ by virtue of the restriction to systems of the same generalized shape, two propositions of practical interest can be deduced, as shown below.

1. PROPOSITION I

When $N = k+1$, that is, when the number of different kinds of physical quantity entering the problem exceeds the number of fundamental units by one, as frequently occurs in practice, the unknown function ϕ reduces to a pure number, and is therefore constant.

If when N is greater than $k+1$, the arguments $\Pi_1 \cdots \Pi_j$ entering the unknown function can be constructed solely from the external variables $q_1 \ldots q_n$, which are independent of temperature, ϕ can be treated as a constant with respect to temperature.

Again, if one or more of the arguments entering the unknown function does contain the linear magnitude L or properties $p_1 \cdots p_m$ it may, in some applications, be found upon inspection that these quantities tend to balance one another in such a way that the net effect of temperature on the product in question can be neglected with a satisfactory degree of approximation. This possibility is especially noteworthy in problems where it can be shown that the product or products affected have only a slight influence on the value of ϕ.

In any case where ϕ can be treated as a constant with respect to temperature it will be denoted by ϕ_o and equation (27) becomes

$$Q_o = \phi_o \cdot Q_1^{-\alpha_o} Q_2^{-\beta_o} \ldots Q_k^{-\kappa_o} \tag{28}$$

Changing over to the classified notation we obtain for P the continued product

$$P = \text{const. } L^{x_o} p_1^{x_1} \cdots p_m^{x_m} q_1^{y_1} \cdots q_n^{y_n} \tag{29}$$

in which $x_o \cdots x_m$ denote the numerical exponents of the internal variables and $y_1 \cdots y_n$ those of the external variables. The number of factors, $m+n+1$, can not exceed the number of fundamental units, k.

Differentiating equation (29) logarithmically and making use of the fact that $q_1 \cdots q_n$ are uninfluenced by changes of temperature, we find that

$$\dot{P} = x_o \dot{L} + x_1 \dot{p}_1 + \cdots + x_m \dot{p}_m \tag{30}$$

Comparing equation (30) with equation (23) it is evident that $C_o = x_o$, $C_1 = x_1, \cdots C_m = x_m$.

Thus whenever the unknown function ϕ can be treated as a constant with respect to temperature, the coefficients entering equation (23) may be found by inspection without the aid of experiment.

2. PROPOSITION II

In the general case where ϕ must be treated as a variable the coefficients of $\dot{L}$, $\dot{p}_1 \cdots \dot{p}_m$ entering the formula for $\dot{P}$, equation (23), can not be determined solely by computation. Two methods are available, however, mathematically identical in substance, one graphical and the other analytical, by which the experimental work can be reduced to a minimum.

(*a*) Graphical Method.—Let K denote the slope, at any point, of an isothermal curve obtained by plotting $\log \Pi_o$ as ordinate against $\log \Pi$ as abscissa, where Π_o and Π are defined by equations (25) and (26). If the function ϕ has only one argument, Π, we have

$$\Pi_o = \phi(\Pi) \tag{31}$$

so that equation (27) can be written

$$Q_o = Q_1^{-\alpha_o} Q_2^{-\beta_o} \cdots \phi(\Pi) \tag{32}$$

Differentiating to obtain the temperature coefficient of the property P which is represented by Q_o in the foregoing notation, we find

$$\dot{Q}_o = -\alpha_o \dot{Q}_1 - \beta_o \dot{Q}_2 - \ \ldots \ + \left(\frac{d \log \phi}{d \log \Pi}\right) \dot{\Pi} \tag{33}$$

But from equation (31) $\phi = \Pi_o$, so that $d \log \phi / d \log \Pi$ is equal to the slope K; and from equation (26), $\dot{\Pi} = \dot{Q} + \alpha \dot{Q}_1 + \beta \dot{Q}_2 + \ \ldots$; therefore

$$\dot{Q}_o = K\dot{Q} + (\alpha K - \alpha_o)\dot{Q}_1 + (\beta K - \beta_o)\dot{Q}_2 + \ \ldots \tag{34}$$

The same result can be obtained by putting equation (31) in the form $\Pi_o \propto \Pi^K$, substituting from equations (25) and (26), differentiating and solving for $\dot{Q}_o$, treating K as a constant in the immediate vicinity of any given point on the curve.

In the rare event when we are obliged to deal with more than one argument Π, this result will be replaced by a summation of terms on the right-hand side, in which K denotes in succession each one of the partial derivatives.

The simplification accomplished by equation (34), as compared to equation (23), consists in three facts:

(1) The experiments can be performed on geometrically similar models, if preferred, instead of on the original system of bodies.[7]

(2) Only one quantity need be varied in conducting the isothermal observations; therefore if more than one quantity can conveniently be varied, an absolute check is available.

(3) The quantity selected for experimental variation need not necessarily be the linear dimension or one of the properties of the component materials, since, if preferred, any one of the external variables entering the product will serve equally well.

(*b*) Analytical Method.—If Q_1 and Q_2 are any two quantities that occur in either or both of the dimensionless products Π_o and Π, the remaining products being held constant for the time, it follows from the relation connecting the derivatives of physical quantities (7) that

$$\frac{\partial \log Q_o}{\partial \log Q_1}=\left(\frac{\alpha}{\beta}\beta_o-\alpha_o\right)+\left(\frac{\alpha}{\beta}\right)\frac{\partial \log Q_o}{\partial \log Q_2} \tag{35}$$

In applying this formula to equation (23), Q_o is taken as before to represent P, while Q_1 represents any one of the internal variables L, $p_1 \ldots p_m$, and Q_2 may represent either an internal or an external variable; that is, it may be allowed to represent any one of the quantities L, $p_1 \ldots p_m$, $q_1 \ldots q_n$, subject to the restrictions discussed in the reference cited (7).

In practice the values of α_o, β_o, α, and β are found by inspection upon comparing the actual dimensional expression for the property P with the symbolic expression given by equations (25) and (26), while the value of the partial derivative $\partial \log Q_o/\partial \log Q_2$ is obtained from the isothermal observations.

The use of equation (35) in conjunction with equation (23) has the same ultimate advantages as the use of the graphical formula (34) and should give the same result; therefore, in any particular application one method can be employed as a check on the other.

V. EXAMPLES SOLVED BY DIMENSIONAL ANALYSIS ALONE

1. PERIOD OF A PENDULUM

Let T denote the period of any rigid compound pendulum of heterogeneous construction, whose generalized shape might be specified by various length ratios and density ratios $r_1 \ldots r_l$. Then if g denotes the acceleration of gravity, while L represents any chosen linear dimension,

$$T=f(L, g, r_1 \ldots r_l) \tag{36}$$

[7] The requisite conditions have been fully discussed by Buckingham (5) and consist essentially in securing the same value of Π for both model and original.

in which the function f will be considered unknown. Applying the Π-theorem;[8] that is, rewriting equation (36) in the standard Π-theorem form which involves dimensionless variables only and then solving for T, we obtain

$$T=\sqrt{\frac{L}{g}}\,\phi\,(r_1\cdots r_l) \tag{37}$$

To a high degree of approximation for small changes in temperature the generalized shape may be treated as a constant with respect to temperature, and since g, being an external variable, is also independent of temperature, we find simply

$$\dot{T}=\frac{1}{2}\dot{L} \tag{38}$$

This example, therefore, is an illustration of Proposition I and might have been solved by direct substitution in equation (30), taking $P=T$, $L=L$, and $x_o=1/2$.

2. SPRING STIFFNESS (PURE BENDING OR TWISTING)

For springs of irregular shape, such that no detailed formula equivalent to equation (2) is available, we can write, in the case of pure bending,

$$S=f(L,\ E,\ r_1\cdots r_l) \tag{39}$$

in which f is an unknown function, while L denotes a linear dimension, and E denotes Young's modulus either at some arbitrary point in the material or the mean value throughout. The length ratios and ratios of Young's modulus, $r_1\cdots r_l$, taken together, serve to define the generalized shape of the spring. By dimensional analysis, as before, equation (39) becomes

$$S=LE\phi\,(r_1\cdots r_l) \tag{40}$$

in which ϕ is an unknown function. Treating the generalized shape as a constant with respect to temperature, which permits a moderate but not an excessive departure from the homogeneous, isotropic condition due to rolling, stamping, or heat treatment, we have

$$\dot{S}=\dot{L}+\dot{E} \tag{41}$$

This result also might have been obtained from equation (30) by substituting $P=S$, $L=L$, $p_1=E$, $x_o=1$, and $x_1=1$.

If instead of pure bending we have a spring deformed by pure twisting or shearing, the solution is the same as before, except that Young's modulus E will be replaced by the shear modulus μ in equations (39) to (41).

The solution for the torsional stiffness of a vertical suspension (wire, ribbon, or fiber) of any cross-sectional form can be shown by

[8] See references (4) and (5). The Π-theorem can be applied by inspection after a little practice if the dimensions of the various quantities are first written down for ready comparison. Further information on the method of dimensions will be found in references (8), (9), (10), and (11).

dimensional analysis to be the same as was given for the circular wire in equation (8).

The solution for complex stresses, that is, where bending and shearing deformations occur simultaneously, can not be obtained from dimensional analysis alone without experimental data and will, therefore, be treated later as an application of Proposition II.

3. ELECTRICAL AND THERMAL RESISTANCE

Let R denote the resistance of any electrically conducting body of irregular shape for which the detailed formula is not available; then if L, as before, represents a linear dimension of this conductor, while the resistivity of the material is denoted by ρ,

$$R=f(L, \rho, r_1 \cdots r_i) \tag{42}$$

For conductors of constant shape we obtain from equation (42) by the method of dimensions

$$R=\frac{\rho}{L} \cdot \phi_o \tag{43}$$

where ϕ_o is a constant, and, therefore

$$\dot{R}=\dot{\rho}-\dot{L} \tag{44}$$

Thus the temperature coefficient of resistance of the body is equal to the temperature coefficient of the volumetric resistivity of the material minus its linear thermal expansivity, a result which can be checked by the usual method of solution in the particular case of any body of simple geometrical form. Equation (44) will be recognized as a consequence of equation (30) if we put $P=R$, $L=L$, $p_1=\rho$, $x_o=-1$, and $x_1=1$.

In the analogous problem of heat conduction the same notation can be employed, R being interpreted as the thermal resistance of the body (temperature drop per unit flow of heat) and ρ as the thermal resistivity of the material (reciprocal of thermal conductivity). In the thermal problem, however, the temperature of the body can not be assumed uniform, since the existence of a finite temperature drop, Δt, is essential to the process of heat conduction.

The material of the thermally conducting body is therefore, in general, nonhomogeneous and departs more and more from homogeneity as the temperature drop increases. Mathematically this signifies that the length ratios and resistivity ratios $r_1 \ldots r_i$ corresponding to any given reference temperature t (for example, the mean temperature of the body or the temperature at the center of the cooler surface) must be recognized as functions of Δt.

If the length ratios are functions of Δt, they must also depend upon the thermal expansion characteristics of the material. Similarly if the resistivity ratios are functions of Δt, they must also depend upon the temperature-resistivity characteristics of the material. Up to moderately large values of the temperature interval Δt these characteristics can be sufficiently defined by the thermal expansivity $\dot{L}$ and

the temperature coefficient of resistivity $\dot{\rho}$, disregarding the variations of $\dot{L}$ and of $\dot{\rho}$ with temperature. Equation (42) can, therefore, be written

$$R=f(L,\ \rho,\ \dot{L},\ \dot{\rho},\ \Delta t) \tag{45}$$

for all bodies having the same generalized shape.

Applying the dimensional method, equation (45) becomes

$$R=\frac{\rho}{L}\phi(\dot{L}\Delta t,\ \dot{\rho}\Delta t) \tag{46}$$

which immediately reduces to equation (43) if $\dot{L}$ and $\dot{\rho}$ are independent of temperature, since Δt is an arbitrary (external) variable and, therefore, likewise independent of temperature. From equation (46), therefore, we obtain the same final result as before, equation (44), for the relative change of resistance R per unit change of the temperature t, although the intermediate steps are different on account of the nonuniform temperature distribution.

VI. EXAMPLES SOLVED WITH THE AID OF ISOTHERMAL EXPERIMENTS

1. VENTURI AIR-SPEED INDICATOR

Let p denote the differential pressure (or suction) generated either by the Venturi-static or Venturi-Pitot instrument on an aircraft traveling at a speed v through air of density ρ and let P denote the dimensionless performance characteristic $p/\rho v^2$.

While the instrument dials are graduated for various air densities on the assumption that P is a constant, it has been found that more accurate results can be obtained by treating P as a function of viscosity (12, 13).

To investigate the effect of temperature on the performance characteristic P for tubes of any given geometrical shape, we can begin by writing

$$P=f(L,\ \mu,\ \rho,\ v) \tag{47}$$

in which L denotes a linear dimension, as, for example, the throat diameter, and μ denotes the viscosity of the air.

From equation (47) by dimensions

$$P=\phi\left(\frac{Lv\rho}{\mu}\right) \tag{48}$$

Differentiating and following the same procedure as was employed in deriving equation (34) from equation (31), we obtain

$$\dot{P}=K(\dot{L}+\dot{\rho}-\dot{\mu}) \tag{49}$$

where K denotes the slope at any point of the graph obtained by plotting observed values of log P against log $(Lv\rho/\mu)$ at constant temperature.

Equation (49) will be recognized as an application of the graphical method, equation (34), taking $Q_o=P$, $\Pi_o=P$, $\Pi=Lv\rho/\mu$, $Q=L$, $Q_1=\rho$, $Q_2=\mu$, $\alpha_o=0$, $\beta_o=0$, $\alpha=1$, and $\beta=-1$.

The same result can be obtained in the following manner by the analytical method, equations (23) and (35). In equation (23) let $P=P$, $L=L$, $p_1=\rho$, $p_2=\mu$;

$$\therefore \dot{P}=C_o\dot{L}+C_1\dot{\rho}+C_2\dot{\mu} \tag{50}$$

in which

$$C_o=\frac{\partial \log P}{\partial \log L} \tag{51}$$

$$C_1=\frac{\partial \log P}{\partial \log \rho} \tag{52}$$

$$C_2=\frac{\partial \log P}{\partial \log \mu} \tag{53}$$

Obviously, a more convenient variable for experimenting than L, ρ, or μ will be the speed, v, since this is an external variable not involving any alteration of the body under test. We, therefore, seek to obtain, if possible, equivalent expressions for C_o, C_1, and C_2 in terms of the isothermal slope $\partial \log P/\partial \log v$, to replace the expressions given by equations (51) to (53).

In equation (35) let $Q_o=P$, $Q_2=v$, $\beta_o=0$, and $\beta=1$ throughout the following analysis, while for the purpose of evaluating C_o we take $Q_1=L$, $\alpha_o=0$, $\alpha=1$; for evaluating C_1 take $Q_1=\rho$, $\alpha_o=0$, $\alpha=1$, and for evaluating C_2 take $Q_1=\mu$, $\alpha_o=0$, $\alpha=-1$.

Substituting these values successively in equation (35) gives

$$\frac{\partial \log P}{\partial \log L}=\frac{\partial \log P}{\partial \log v}=C_o \tag{54}$$

$$\frac{\partial \log P}{\partial \log \rho}=\frac{\partial \log P}{\partial \log v}=C_1 \tag{55}$$

$$\frac{\partial \log P}{\partial \log \mu}=-\frac{\partial \log P}{\partial \log v}=C_2 \tag{56}$$

Substituting in equation (50) the values of C_o, C_1, and C_2 given by equations (54) to (56)

$$\dot{P}=\left(\frac{\partial \log P}{\partial \log v}\right)(\dot{L}+\dot{\rho}-\dot{\mu}) \tag{57}$$

This result confirms equation (49), since when L, ρ, and μ are held constant the slope K, representing $d \log P/d \log (Lv\rho/\mu)$ reduces to $\partial \log P/\partial \log v$.

If we write $P \propto v^n$ as an approximation for a limited range of speeds, it follows that $K=n$. Now the exponent n would be expected to lie between the limits of 0 for completely turbulent fluid motion (large throat diameter, high speed, and low altitude) and -1 for stream-line motion (small throat diameter, low speed, high altitude). For practical purposes $\dot{L}$ can be neglected in comparison with $\dot{\rho}$ and $\dot{\mu}$. Treating the atmosphere as an ideal gas of absolute temperature θ, we find $\dot{\rho}=-1/\theta$. Also as a fair approximation from $-40°$ to $+40°$

C., it has been shown (14) that $\dot{\mu} = +(4/5)\ (1/\theta)$. Equations (49) and (57), therefore, reduce to the approximate form

$$\dot{P} = -\frac{9}{5}\left(\frac{K}{\theta}\right) \tag{58}$$

in which K is a negative number (ranging from 0 to -1), so that $\dot{P}$ is always positive.

2. SPRING STIFFNESS (COMPLEX STRESSES)

When the shear modulus μ is added to the list of quantities already included in the stiffness problem, we obtain in place of equation (40) for all springs of the same generalized shape

$$S = LE\phi\left(\frac{\mu}{E}\right) \tag{59}$$

Differentiating leads to the result

$$\dot{S} = \dot{L} + (1 - K)\dot{E} + K\dot{\mu} \tag{60}$$

in which K is the slope of the graph obtained when the observed values of log (S/LE) are plotted against log (μ/E) at constant temperature.

Equation (60) can also be derived by direct substitution in equation (34), taking $Q_o = S$, $\Pi_o = S/LE$, $\Pi = \mu/E$, $Q = \mu$, $Q_1 = L$, $Q_2 = E$, $\alpha_o = -1$, $\beta_o = -1$, $\alpha = 0$, and $\beta = -1$.

An equivalent result in analytical form can be obtained by making the appropriate substitutions in equations (23) and (35).

If Poisson's ratio is used in place of μ/E in equation (59), we find (1)[9] with the aid of equations (12) and (13)

$$\begin{aligned}\dot{S} &= \dot{L} + C\dot{E} + C\dot{\sigma} \\ &= \dot{L} + \left[1 + C\left(\frac{1+\sigma}{\sigma}\right)\right]\dot{E} - C\left(\frac{1+\sigma}{\sigma}\right)\dot{\mu}\end{aligned} \tag{61}$$

in which C is the slope of the graph obtained by plotting log (S/LE) against log σ.

3. VIBRATION FREQUENCY OF A LOADED SPRING (ELASTIC PENDULUM)

A stiff spring having its natural frequency reduced by the addition of a localized mass m, has been used as a working standard for time intervals intermediate between the period of a tuning fork and that of a gravity pendulum.

If the stiffness of the spring can be measured at the effective point of application of the mass m, it can be shown by the method of dimensions that the frequency is given by

$$n = \sqrt{\frac{S}{m}}\,\phi\left(\frac{m_o}{m}\right) \tag{62}$$

[9] See equation (7) of reference cited.

in which m_o denotes the mass of the spring itself. From equation (62) we readily find

$$\dot{n}=\frac{1}{2}\dot{S} \tag{63}$$

since evidently m and m_o are unaffected by temperature. Substituting from equation (60) into equation (63) gives

$$\dot{n}=\frac{1}{2}\dot{L}+\frac{1}{2}(1-K_s)\dot{E}+\frac{1}{2}K_s\dot{\mu} \tag{64}$$

in which K_s is identical with K of equation (60), the subscript being attached to call attention to the fact that the value is to be obtained from observations of stiffness rather than of frequency.

A more general solution can be obtained without reference to equation (62) as follows: Starting with a qualitative statement for systems of fixed generalized shape, we can write

$$n=f(L, E, \mu, \rho, m) \tag{65}$$

in which ρ denotes the density of the spring material, the other quantities having the same interpretation as before. Then applying the method of dimensions to equation (65) we obtain

$$n=\frac{1}{L}\sqrt{\frac{E}{\rho}}\,\phi\left(\frac{\mu}{E}, \frac{m}{\rho L^3}\right) \tag{66}$$

It now appears immediately that the argument $m/\rho L^3$ is unaffected by temperature, since m is essentially independent of temperature, while $\dot{\rho}=-3\dot{L}$; differentiating, therefore, and disregarding $m/\rho L^3$, we find that

$$\dot{n}=\frac{1}{2}\dot{L}+\frac{1}{2}(1-2K)\dot{E}+K\dot{\mu} \tag{67}$$

in which K is the slope of the graph obtained by plotting log $(nL\sqrt{\rho/E})$ against log (μ/E). This result agrees with equation (64) when K_s is put equal to $2K$, a relationship which can be deduced from the definitions of K_s and K in conjunction with equation (62).

Equation (67) can also be obtained by direct substitution in equation (34) after extending the latter to include the term $(\gamma K-\gamma_o)\dot{Q}_3$ and then putting $Q_o=n$, $Q=\mu$, $Q_1=L$, $Q_2=E$, $Q_3=\rho$, $\alpha_o=1$, $\alpha=0$, $\beta_o=-1/2$, $\beta=-1$, $\gamma_o=1/2$, and $\gamma=0$, and an equivalent result can be obtained, as in the two preceding examples, by making the appropriate substitutions in equations (23) and (35).

Turning back to the telephone diaphragm problem, it is interesting to note that equation (13) is a special case of equation (67) for which K has the particular value $-3/7$.

4. COEFFICIENT OF FRICTION OF A LUBRICATED JOURNAL BEARING

As an example of a system which does not conform to the usual condition of geometrical similarity,[10] consider the energy dissipated

[10] Sometimes erroneously assumed to be a prerequisite for the application of the method of dimensions.

in the oil film which occupies the clearance space of a well-lubricated journal bearing. In general the oil film is not of a uniform thickness circumferentially, this being due to the eccentricity of the journal, which in turn depends on the viscosity of the oil, μ, the speed of rotation, n, and upon the total load, W. There may also be a varying amount of cavitation at the open ends of the bearing; that is, the oil may not completely fill the clearance space between the journal and the bearing, even when liberally supplied. Nevertheless, under these conditions a simple relation has been found by the method of dimensions (15) which can be written

$$f_o = \phi\left(\frac{\mu n L^2}{W}\right) \tag{68}$$

In equation (68) f_o is the coefficient of friction and L is the length of the bearing, the subscript having been attached to represent the particular case in which the materials of both journal and bearing have the same thermal expansivity.

Differentiating, we obtain as was first shown by equation (22)

$$\dot{f}_o = \left(\frac{\partial \log f_o}{\partial \log L}\right)\dot{L} + \left(\frac{\partial \log f_o}{\partial \log \mu}\right)\dot{\mu} \tag{69}$$

From equation (68) either by inspection of by substituting in equation (35), selecting n as the most convenient variable for experimental control,

$$\frac{\partial \log f_o}{\partial \log L} = 2\frac{\partial \log f_o}{\partial \log n} \tag{70}$$

$$\frac{\partial \log f_o}{\partial \log \mu} = \frac{\partial \log f_o}{\partial \log n} \tag{71}$$

$$\therefore \dot{f}_o = \left(\frac{\partial \log f_o}{\partial \log n}\right)(2\dot{L} + \dot{\mu}) \tag{72}$$

or very approximately on account of the linear expansivity of the metal being small compared to the temperature coefficient of viscosity of the oil,

$$\dot{f}_o = \left(\frac{\partial \log f_o}{\partial \log n}\right)\dot{\mu} \tag{73}$$

Proceeding to the case of dissimilar metals where a still further departure from geometrical similarity occurs, we may consider first the effect of differential expansion on the clearance, C (difference between bearing diameter and journal diameter). If $\Delta\dot{L}$ denotes the difference between the thermal expansivity of the bearing metal and that of the journal, while the diameter of the journal is represented by D, we have

$$C \gtrless \left(\frac{D}{C}\right)\Delta\dot{L} \tag{74}$$

according as the bearing metal is free to expand without opposition, or restricted in some degree by stresses that are set up.

While the connection between coefficient of friction and clearance can not be obtained from dimensional analysis, the following relation expressing the shearing resistance of a uniform film may be applied as a reasonable approximation for the purpose of computing the effect of small changes in temperature, viz:

$$f \propto \frac{1}{C} \tag{75}$$

Differentiating equation (75) we obtain for $\Delta\dot{f}$, the increment which must be added to equation (73) to take account of the change in clearance due to a rise of temperature,

$$\Delta\dot{f} = -\dot{C} \tag{76}$$

Referring to equation (74) and taking the equality sign as representing the maximum effect, substituting in equation (76) and adding the result to equation (73) gives finally

$$\dot{f} = \left(\frac{\partial \log f}{\partial \log n}\right)\dot{\mu} - \left(\frac{D}{C}\right)\Delta\dot{L} \tag{77}$$

Both terms on the right of equation (77) are normally negative for an oil-lubricated bearing operating on the stable side of the minimum coefficient of friction value, since $\dot{\mu}$ is negative and $\Delta\dot{L}$ positive. For an air-lubricated bearing $\dot{\mu}$ is positive.

The first term on the right of equation (77) has been readily obtained by the same methods demonstrated in the three examples immediately preceding. The second term will serve as a particular illustration of the general statement made in the paragraph following equation (23) regarding effects due to change of shape which can be calculated by conventional methods and then superposed on the solution obtained for a system of constant shape.

VII. EXTENSION TO DETERMINE THE EFFECT OF PHYSICAL CONDITIONS OTHER THAN TEMPERATURE

The variable quantity t which has thus far been taken to represent the temperature is in fact entirely arbitrary and can equally well be interpreted as hydrostatic pressure, electrostatic, or magnetic field intensity, or any other measurable condition on which the properties of the system may depend. Temperature, however, can never (on the absolute scale) be made equal to zero, and, in general, for practical reasons, whatever other factor is investigated in any particular problem the temperature factor must be considered in addition.

As an example of the effect of pressure equation (44) may be written

$$\dot{R}_p = \dot{\rho}_p - \dot{L}_p \tag{78}$$

in which $\dot{R}_p$ denotes the relative increase in the electrical resistance of a body per unit increase of hydrostatic pressure; $\dot{\rho}_p$ the pressure

coefficient of resistivity of the material and $(-\dot{L}_p)$ its linear compressibility. Replacing $(-\dot{L}_p)$ by its equivalent $(+k/3)$, where k is the ordinary volumetric compressibility, equation (78) becomes

$$\dot{R}_p = \dot{\rho}_p + \frac{k}{3} \qquad (79)$$

Rewriting equation (44) with subscript t indicating temperature effects,

$$R_t = \dot{\rho}_t - \dot{L} \qquad (80)$$

From equations (79) and (80) we obtain for the change of resistance due to a simultaneous temperature rise Δt and pressure increase Δp

$$\frac{\Delta R}{R} = (\dot{\rho}_t - \dot{L})\Delta t + \left(\dot{\rho}_p + \frac{k}{3}\right)\Delta p \qquad (81)$$

Equation (81) also enables us to compute either one of the coefficients $\dot{\rho}_t$ or $\dot{\rho}_p$ from a knowledge of the other when the expansivity and compressibility of the material are given and the actual change of resistance is observed.

VIII. FURTHER QUESTIONS FOR INVESTIGATION

A logical continuation of the present study might proceed along somewhat the following lines:

(*a*) Further practical applications.
(*b*) Compilation of tables of data for the requisite thermal coefficients, such as $\dot{L}$, $\dot{E}$, $\dot{\mu}$, etc.
(*c*) Formulation of precedure for computing $\dot{r}_1 \cdots \dot{r}_l$ for systems of variable generalized shape.
(*d*) Extension to bodies of nonuniform temperature.
(*e*) Extension to include the effect of large changes in temperature.
(*f*) Extension to other physical observations besides properties of bodies.

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THE NEUTRALIZATION OF SPACE CHARGE BY POSITIVE IONS IN CAESIUM VAPOR

By V. E. Whitman

ABSTRACT

A tube was constructed in which the neutralization of space charge by positive ions was studied. The positive ions were formed by the photo-electric ionization of caesium vapor. The change in current due to the illumination was measured as a function of such controllable variables as pressure, light intensity, anode voltage, and cathode emission. An empirical relation between change in anode current and illumination is given which may be fitted to the experimental results by adjusting one constant.

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I. INTRODUCTION

1. HISTORICAL

The maximum current which can be carried by ions or electrons between electrodes is determined by the form of the electrodes, the potential difference between them, the mass or the ion or electron, and the charge it carries. The flow of current is said to be limited by space charge.

From the viewpoint of theory and experiment taken together, the geometrical arrangement which lends itself best to investigation is that of concentric cylinders with the inner as cathode. Such an arrangement is usually sealed in a highly exhausted inclosure. The cathode, in general, consists of a wire which is heated by the passage of an electric current and thus made to emit electrons.

In high vacuum thermionic devices of the type in which the anode is a flat plate, the few positive ions formed play an insignificant part in the conduction. Under ordinary conditions they move over to the cathode and discharge or else move out from the field between the electrodes. In neither case do they contribute appreciably to the neutralization of the electron space charge.

If, however, the thermionic device is made so that the cathode lies along the axis of a cylindrical anode with closed ends except where the cathode leads must penetrate any positive ion which is formed within the inclosure, having a component of velocity transverse to the radius of the cylinder, will, in general, not fall directly into the cathode, but

will perform some type of orbit within the field. Moreover, the closed end construction referred to will greatly reduce the chances of the ion wandering from the inclosure. Such an imprisoned ion will execute orbits to-and-fro across the tube as long as it has any component of velocity transverse to the radius. This necessary transverse velocity is present in the thermal agitation of the atoms.

The more excursions a positive ion makes across the tube before it strikes the cathode, the more effective it is in neutralizing the space charge. The condition that a positive ion starting from a point immediately inside of the anode shall just fail to strike the cathode is that V, the potential difference between anode and cathode shall be less than the value given by

$$e\ V=\frac{1}{2}\ mv_o^2\left(\frac{R}{r}\right)^2 \tag{1}$$

In this equation, as given by Hull[1] m is the mass and e the charge on the ion, v_o the initial transverse velocity, and R and r the radius of anode and cathode, respectively.

Within the range of conditions for which equation (1) is valid we see that (1) for given V and $\frac{R}{r}$ the proportion of ions which will fail to reach the cathode on their first trip is the same for all gases at the same temperature; and (2) the higher the temperature of the gas in the tube, the greater will be the average value of $\frac{1}{2}\ m\ v_o^2$ and the greater will be the proportion of ions missing the cathode.

Kingdon[2] used a tube in which a cylindrical anode practically surrounded the electron-emitting portion of a concentric hot wire cathode, and worked with He, H, Ne, and Hg at pressures ranging from 10^{-2} to 10^{-7} mm. The effectiveness of a positive ion in neutralizing the space charge was found to vary as the 2/3 power of $\frac{1}{p}$. Over the range of pressures used, the results were consistent with the assumption that the recombination of positive ions with electrons was negligible.

Now the contribution to the space charge by a particle carrying a charge is proportional to the time τ consumed in making the trip between the electrodes once times the number of trips. Approximate calculations showed that in one of the tubes used by Kingdon with helium (τ_+) for the ion was about 1.4×10^{-6} secs. and (τ_-) for the electron was about 1.08×10^{-8} seconds for $V=35$ volts. Hence, one ion moving once from anode to cathode will neutralize the space charge of $\tau_+/\tau_-=130$ electrons. This number of electrons in excess of the normal space-charge current will then flow across the tube. A calculation led Kingdon to believe that in He at 10^{-5} mm, an ion which just missed the filament on its first passage across the tube might travel across the tube as many as 350 times before losing its energy and discharging to the cathode. It is thus conceivable that one helium atom might neutralize the space charge effect of as many as 4.5×10^4 electrons in the type of tube used by Kingdon.

[1] Hull, Phys. Rev., 18, p. 31; 1921.

[2] Phys. Rev., 21, p. 408; 1923.

Foote and Mohler[3] utilized this effect for measuring the photoelectric ionization of caesium vapor. The form of tube used was similar to that shown in Figure 1 except that no electrical shielding was provided. The left-hand end of the tube was fitted with a plane quartz window through which light of various wave lengths was passed into the anode cylinder. A gauze at the left-hand end of the anode cylinder served to effectively imprison the positive ions formed. The filament was run at a temperature high enough so that the current to the anode would be limited by space charge, but sufficiently low so that the filament would not emit positive ions.

Under these conditions, current-voltage characteristics of the tube were obtained when the space between anode and cathode was illuminated with light of various wave lengths. Over the range of vapor pressures covered, the change in thermionic current on illumination was found to increase with the pressure, as shown in Table 1.

TABLE 1.—*Change in current due to radiation as a function of vapor pressure*

Temperature, ° C.	Pressure in mm Hg	Δi
		Amps.
95	0.00048	$0.7\times10-5$
108	.001125	$1.1\times10-5$
135	.0073	$2.0\times10-5$
145	.0090	$2.2\times10-5$
170	.0313	$3.2\times10-5$

The vapor pressures were calculated from the temperature measurements using the work of Langmiur and Kingdon.[4]

The increase in thermionic current due to illumination was found to increase with larger filament emission.

The change in current with radiation was found to be nearly independent of voltage below the ionization potential, but to approach zero rapidly when ionization by electron impact occurred.

This work was continued in a second paper by Mohler, Foote, and Chenault,[5] in which the relative photosensitivity—that is, the ions per unit intensity—was investigated as a function of the wave length.

Throughout this work it was assumed, and experimentally verified, that the change in current due to radiation was directly proportional to the intensity of the radiation. This was over a relatively low range of intensities. It is evident that if the intensity were increased indefinitely, the effect of space charge would finally be completely wiped out, after which a further increase in intensity would have no effect on the current. The theoretical aspects of this nonlinear relation at high intensities become too complicated to allow much analytical investigation of the phenomenon.

In some unpublished experiments Mohler used a beam of electrons as the ionizing source. He found that particularly at low pressures, and over a limited range of ion currents, fairly reliable values could be gotten of the absolute number of electrons released from the cathode region by one positive ion.

[3] Phys. Rev., **26**, 195; 1925. [4] Proc. Roy. Soc., **107A**, p. 61; 1925. [5] Phys. Rev., **27**, p. 37; 1926.

2. PRELIMINARY MEASUREMENTS

Because of the incompleteness of the available experimental data it was thought desirable to investigate the phenomenon of the neutralization of space charge by positive ions, throughout a greater range of experimental conditions than had heretofore been recorded. Some differences should be noted between the conditions under which Kingdon's[6] experiments and those described here were performed. In the present work there were probably no true ion orbits as analyzed by Kingdon. In the experiments to be described, higher pressures and lower voltages were used than by Kingdon. It was decided to use radiation rather than electrons as the source of ionization because of the greater reliability of the results over the range of variables investigated. The use of radition has one disadvantage, namely, that there is no way approaching reliability with which the absolute number of ions present can be calculated. A rough estimate may be obtained from some recent absolute measurements of photoionization to be published shortly by Mohler and Boeckner. From this work it appears that the ion current is of the order of 10^{-4} times the change in electron current.

X rays from a molybdenum tube of the Collidge type were first tried as the ionizing source. The X-ray tube was run at as near constant output as could be gotten from the power circuits available. The tube in which the space charge was produced and neutralized was caesium filled, and in all respects similar to that used by Foote and Mohler.[7] All other variables were held constant and the change in current due to illumination was measured as a function of the vapor pressure of the Cs. As predicted by Kingdon's theory, the effect at first increased with increasing pressure. With 33,000 r. m. s. volts across the X-ray tube, and a current consumption of 15 milliamperes, the change in current in the caesium tube due to illumination with the X rays became a maximum at a vapor pressure of caesium of 0.43 mm. of mercury. Above this pressure, the change was less.

These experiments were sufficient to prove that the effect with X rays was real, but small for the intensities of X rays available. Difficulty was also experienced in shielding the galvanometer system from electrical disturbances arising in the high tension X-ray tube circuit.

Light from a concentrated filament lamp was chosen as the source of ionization in the subsequent experiments because of the high intensities available, and because of the ease with which its intensities could be controlled and reproduced. The original caesium tube had to be abandoned because it contained a relatively low resistance electrical leak between anode and cathode.

II. APPARATUS

A tube of the design shown in Figure 1 was made. This was not essentially different from that originally used except for the addition of the guard ring shown.

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[6] See footnote 2, p. 158.

[7] See footnote 3, p. 159.

The window at the left-hand end of the tube in Figure 1 was a plane piece of clear fused quartz. The anode cylinder was made of platinum and measured approximately 3 cm diameter by 10 cm length. The filament was of 5-mil tungsten wire, oxidized before inserting the caesium. The usual precautions of high temperature prolonged baking with pumps running were observed before the caesium was finally distilled into the tube and the tube sealed.

The electrical circuits associated with this tube are also to be seen in Figure 1. By means of the potentiometer arrangement shown at E_3 it was possible to read changes in anode current of the order of 10^{-8} amperes on the galvanometer, while the total anode current might be of the order of 10^{-3} amperes.

A 400-watt lamp of the type used in motion-picture projectors was used as the source of light. A quartz lens was used to render the light passing into the tube approximately parallel. The intensity of the light entering the tube was controlled by inserting one or more nickel gauze screens in the path of the light. Without screens, the light

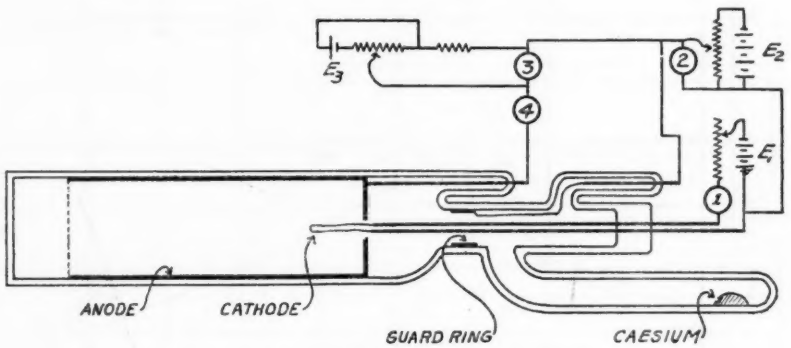

FIGURE 1.—*Tube and associated apparatus*

E_1, E_2, E_3, Batteries.
(*1*) Ammeter. (*2*) Ammeter.
(*3*) Galvanometer. (*4*) Milliammeter.

intensity at the tube was found to be 1,600-foot candles. Each screen was found to have a transmission of 0.25.

The main body of the tube shown was maintained at a temperature not greatly different from 300° C. The temperature of the side tube containing caesium was varied to adjust the vapor pressure. These pressures were calculated from the temperature of the side tube, using the curve selected by Little.[8]

III. METHOD AND RESULTS

Before making any electrical measurements at any pressure, the temperature of the tube was held constant for several hours so that equilibrium might be reached. For the low pressures; that is, low temperatures, as many as 15 hours were allowed for reaching this equilibrium. For the highest pressures only 3 hours were allowed.

Some uncertainty was felt as to just how the filament current should be set so that readings under otherwise different conditions might be

[8] Phys. Rev., **30**, p. 109; 1927.

comparable. Check readings could not be obtained when the same filament current was used at the same vapor pressure of caesium on consecutive days. This was due to the changing emission characteristics of the filament as a result of prolonged high temperature exposure to caesium vapor. The method adopted for setting the filament current was as follows: After pressure equilibrium had been reached, 10 volts were applied between anode and cathode and the filament current increased until the anode current was 1 milliampere. In the single case of the upper curve of Figure 6, the filament temperature was obtained by setting for 15 milliamperes at 10 volts.

With a given filament setting, readings were made of the change in anode current as a function of light intensity for several voltages below the ionization potential of caesium vapor.

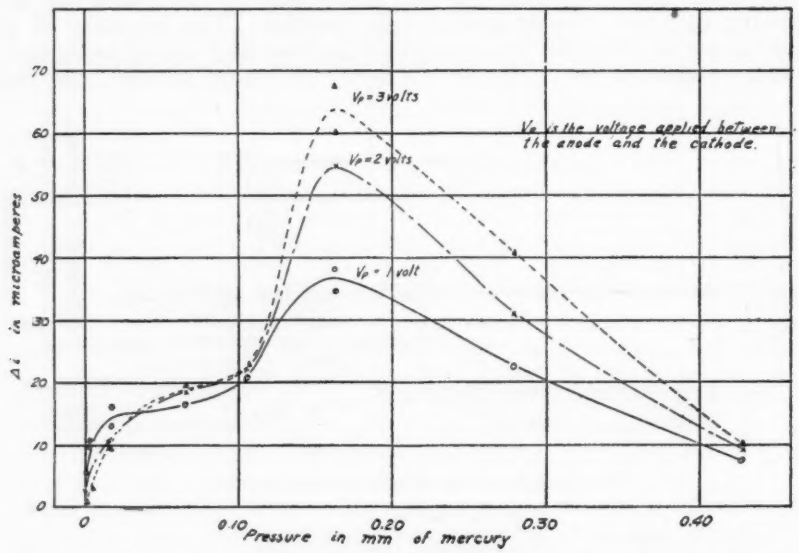

FIGURE 2.—*Variation of Δi, at maximum illumination, with pressure for three different anode voltages*

Preliminary runs showed that the photo-electric effect on the electrodes was negligible; also that the magnetic field set up by the electric heating furnaces had a negligible effect.

Table 2, together with the curves referred to in its last column, give the results of these measurements of Δi, the change in anode current due to illumination with light of intensity I. The table only gives values of Δi for the same maximum illumination, taken as unity in all cases. The points on the curves listed in the right-hand column are for other values of light intensity. Figure 2 showing Δi at various voltages as a function of pressure was plotted from the data contained in Table 2 and its associated curves.

TABLE 2

Pressure of Cs in mm Hg	Anode voltage	Anode current in microamperes	Δ_i in microamperes for I=1.00	$K_3 \times 10^{-9}$	Curve in figure
0.0018	1.0	14.3	5.53	9.1	4
.0039	1.0	10.9	10.87	4.2	5
.0039	3.0	76.0	2.69	4.7	5
.0185	1.0	6.5	16.14	2.74	6
.0185	3.0	41.4	11.68	1.62	6
.0185	3.0	55.8	45.70	.22	6
.066	1.0	2.1	16.20	3.4	7
.066	3.0	14.0	19.50	1.53	7
.164	1.0	3.0	34.6	.77	8
.164	3.0	10.6	63.1	.22	8
.427	1.0	15.9	7.42	5.8	
.427	3.0	41.2	9.83	2.0	

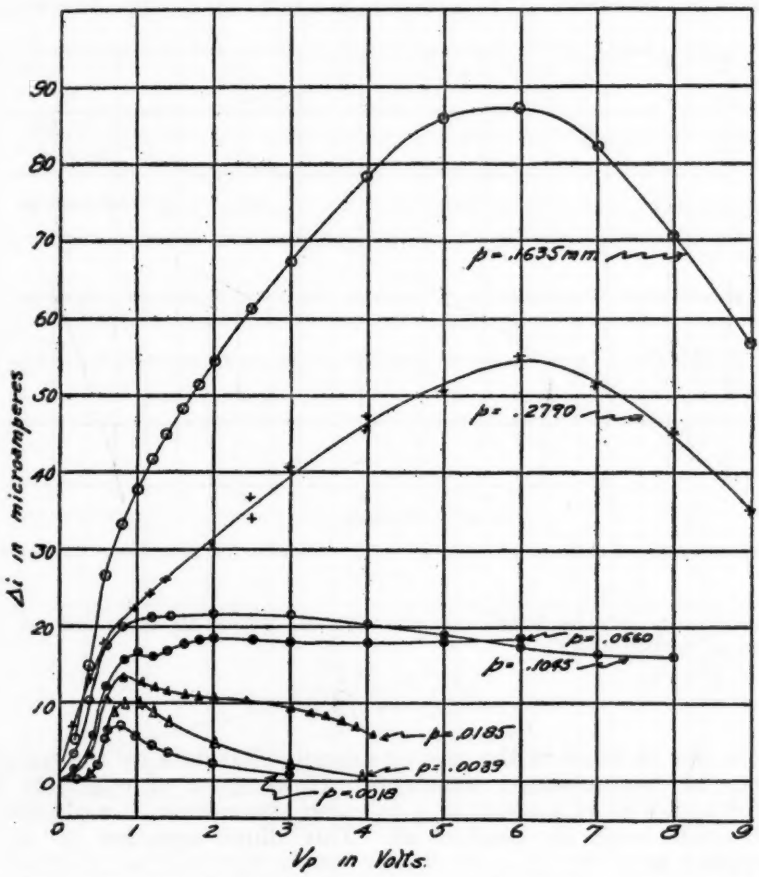

FIGURE 3.—*Variation of Δi, at maximum illumination, with anode voltage, at different pressures*

Using the full intensity of illumination, the change in anode current was investigated as a function of the anode voltage at various pressures. The results of these measurements are given in the curves of Figure 3.

IV. DISCUSSION

A rigorous analytical attack of the problem of the neutralization of space charge by positive ions would involve difficulties out of proportion to the usefulness of the solution if one were possible. It is desirable, however, to present an empirical relation which fits the results.

Let it be assumed that the rate of production of ions is proportional to the intensity I of the light, and that τ is the average life of an ion. Then the number of ions present will be $aI\tau$.

Second, let it be assumed that the change in anode current Δi is proportional to the number of ions present; that is, $\Delta i = baI\tau$.

If it were assumed that the loss of ions is proportional to the concentration, then Δi would be proportional to the intensity I. This is not observed. The addition of a term involving a loss of ions

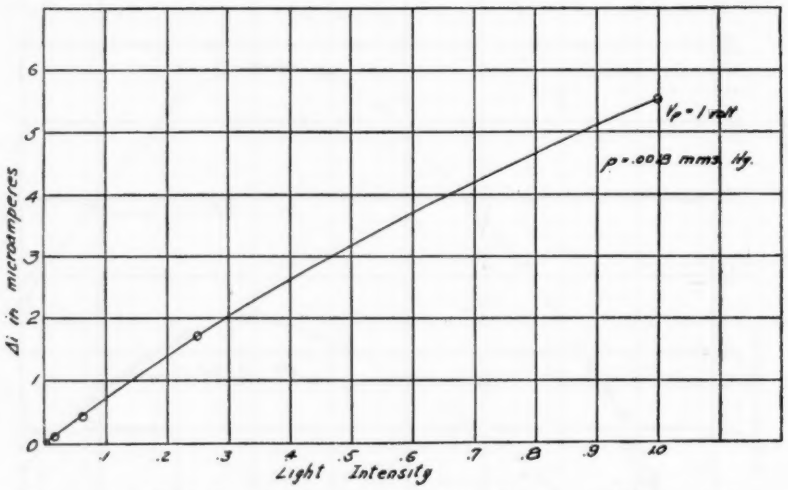

FIGURE 4.—*Variation of Δi, with light intensity for conditions noted on curves*

proportional to the total current $(i+\Delta i)$ gives an equation of the form of equation (2)

$$\Delta i = \frac{baI}{c+d\,(i+\Delta i)} \tag{2}$$

which can be fitted to the present experimental data by the suitable choice of two arbitrary constants. However, c of equation (2), which comes in on account of a diffusion assumption, is negligible in comparison with the product ab. This allows equation (2) to be simplified to

$$\frac{I}{\Delta i} = K_3\,(i+\Delta i) \tag{3}$$

which fits the data within the experimental error, and with the use of only one arbitrary constant.

Figures 4, 5, 6, 7, and 8 are intended to show the agreement between the experiments and equation (3). The points indicated along the curves were experimental determinations. For each condition K_3 was calculated from the value of Δi at $I=1.0$. This was con-

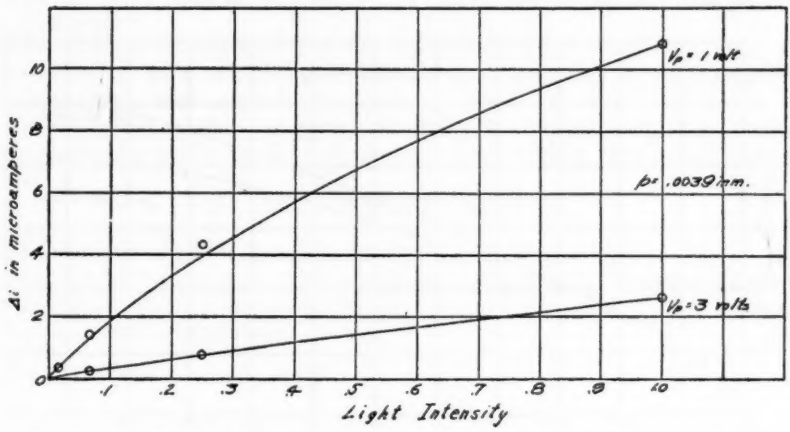

FIGURE 5.—*Variation of Δi, with light intensity for conditions noted on curves*

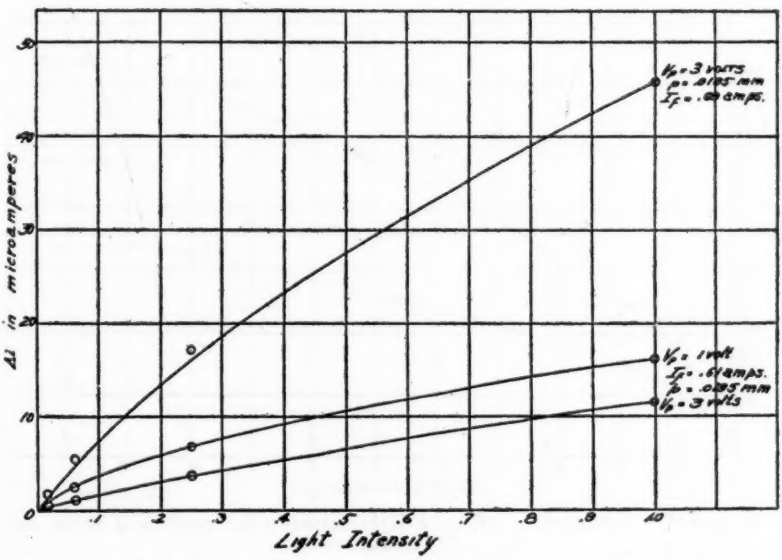

FIGURE 6.—*Variation of Δi, with light intensity for conditions noted on curves*

sidered justifiable because of the greater precision with which Δi could be measured at this intensity. The curves shown in Figures 4, 5, 6, 7, and 8 are calculated from equation (3) using the values of K_3 obtained as outlined above, and given in Table 2.

The agreement as thus presented, is not striking, but as good as might reasonably be expected.

Inspection of the data shows a definite tendency for K_3 to decrease as applied voltage is increased. A definite tendency of K_3 to vary with the pressure is not so obvious.

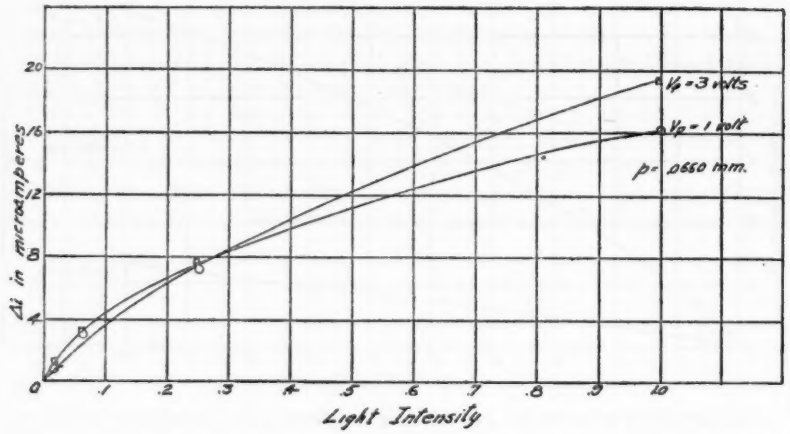

FIGURE 7.—*Variation of Δi, with light intensity for conditions noted on curves*

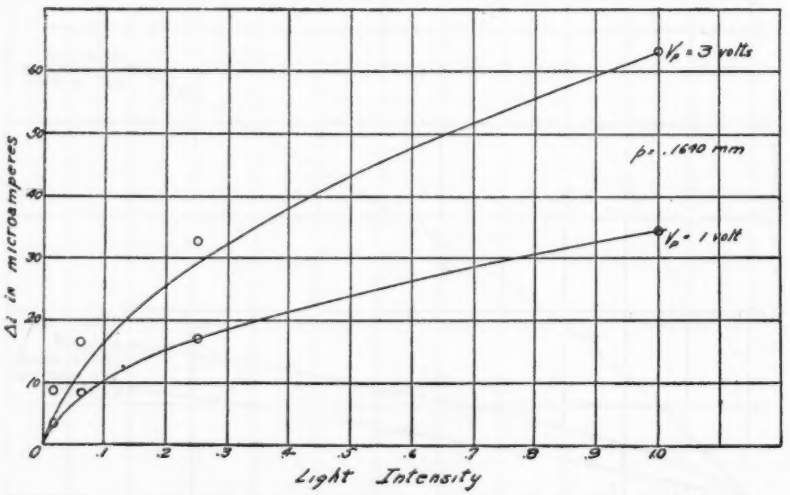

FIGURE 8.—*Variation of Δi, with light intensity for conditions noted on curves*

A loss of ions which will change with the electron current, can be pictured as a flow to the cathode. It would be difficult, however, to prove this loss proportional to the current.

V. CONCLUSIONS

A tube was constructed in which the neutralization of space charge by positive ions was studied.

The positive ions were formed by the photo-electric ionization of caesium vapor.

The change in current due to the illumination was measured as a function of such controllable variables as pressure, light intensity, anode voltage, and cathode emission.

An empirical relation is given which by the choice of a single constant, may be made to fit the observations within the experimental error.

VI. ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to Dr. F. L. Mohler under whose supervision this work was done. Besides placing the facilities of his laboratory at the author's disposal, he has offered many valuable suggestions.

WASHINGTON, June 1, 1929.

REGULARITIES IN THE ARC SPECTRUM OF HAFNIUM (Hf_I)

By William F. Meggers and Bourdon F. Scribner

ABSTRACT

The first regularities among lines characterizing the first spectrum of hafnium (Hf_I) have been discovered. Combinations of seven low energy levels with higher excited states account for more than 200 lines. Inner quantum numbers have been assigned to the energy levels and a tentative identification of the seven low levels is suggested.

As soon as new descriptions of hafnium arc and spark spectra were completed [1] the authors attempted to find regularities among the lines. Our first attempt to classify Hf_I lines was not successful, but a wave-number system containing 206 Hf_{II} lines was established without great difficulty. These first regularities in the spark spectrum of hafnium were published last year.[2] Encouraged by the results obtained with Hf_{II} lines, attention was again turned to the Hf_I lines; a recurring difference of 1,071 cm^{-1} was found, but no further progress was made. It must be remembered that Zeeman effects, temperature classification, absorption data, and similar descriptive information which have aided in the analysis of other complex spectra were entirely lacking for Hf spectra and we had to depend solely on the combination principle as a criterion for classification. Very recently King has published [3] the results of an investigation on the furnace spectrum of hafnium. On account of the high boiling point of Hf, relatively high temperature is required to excite its spectra, and King was able to observe only a small portion of the complete arc spectrum. But King's descriptions of furnace spectra have always been of great importance in the analysis of spectra, and it is a pleasure to testify that this applies also to his results with the Hf_I spectrum.

The general procedure in constructing a wave-number system for a complex spectrum was briefly outlined in our paper on the Hf_{II} spectrum (loc. cit.). In our preliminary attempts to find regularities among Hf^1 lines, we confined attention to differences less than 2,000 cm^{-1}, and thereby unwittingly shut ourselves off from the solution of our problem. When King's data on the furnace spectrum became available we made another attack on the structure of the spectrum by systematically subtracting from each other the vacuum wave numbers of all low-temperature lines (Classes II and III). This immediately led to the recognition of two important wave-number

[1] Meggers, B. S. Jour. of Research (R. P. 8), **1**, p. 151; 1928.
[2] Meggers and Scribner, J. Opt. Soc. Am. & Rev. Sci. Inst., **17**, p. 83; 1928.
[3] King, Astrophys. J. **70**, p. 105; 1929.

intervals, viz, 2,356.6 and 2,211.0 cm^{-1}. These then became the nucleus of a significant wave-number system which by successive addition of other levels finally became the 2-dimensional matrix given in Table 1. In this table the relative values for seven levels (A, B, C . . .) of low-energy content are printed at the top and the derived values for 63 higher states (1, 2, 3, 4 . . .) on the left margin. The level values are followed by a number (inclosed in brackets) which represents the value of the inner quantum number, which has been tentatively assigned to each level. Assuming that our level A has $j=2$, the relative values of the inner quantum numbers for other levels are derived from the observed combinations which appear in the body of the table, remembering that a combination is permitted only for changes of ± 1 or 0 in the value of j. Owing to the relatively small number of low-energy levels which we have thus far established, it is not always possible to assign a final value of j to each of the higher levels, and in such cases corrections may be necessary.

The combinations of energy levels in Table 1 are represented by vacuum wave numbers of observed spectral lines. Above each wave number is the measured wave length, followed (in parentheses) by the estimated intensity and the temperature class. When temperature class accompanies intensity the data are quoted from King; otherwise the intensities are taken from Meggers. In general, King's estimated intensities exceed those of Meggers in the ultra-violet, but are about the same for visible lines. There appears to be a discontinuity in King's temperature classes in the ultra-violet at 2,860 A. All lines of shorter wave length are indicated as belonging to Classes IV or V, but our analysis show that many of these lines involve the low levels which otherwise predominantly give lines of Classes II or III. The tendency for temperature class to increase as the energy of the metastable levels increases is quite marked; it may be regarded as evidence that the levels are correctly oriented. It may be remarked that Table 1 includes a large majority of the stronger Hf_I lines; only one low-temperature line, 3,057.02 A (100 II) remains, and it is quite probable that it is a single combination of a level having $j=5$ with the low C level, $j=4$. The total number of lines classified in Table 1 is 218, four of which have been used twice. The average deviation of the observed wave numbers from the computed differences of the energy levels is only 0.05 cm^{-1}, which corresponds to an average error of less than 2 parts in 1,000,000 in the wave-length determinations of these lines. Somewhat better agreement between observed and calculated wave numbers of Hf_I lines as compared with the classified Hf_{II} lines is due to the fact that the center of gravity of the former group is of greater wave length, for which the same error in wave length corresponds to a smaller error in wave number.

TABLE 1.—*Classified lines in the Hf_I spectrum*

		A 0.00 [2]	B 2,356.60 [3]	C 4,567.58 [4]	D 5,521.64 [0]	E 5,638.55 [2]	F 6,572.50 [1]	G 8,983.70 [2]
		5, 654. 64 (4)		7, 624. 40 (30)				
1	17, 679. 73 [3]	17, 679. 70		13, 112. 18				
		5, 550. 60 (50 III)	6, 386. 23 (6 III)			8, 080. 32 (4)		
2	18, 010. 98 [2]	18, 011. 08	15, 654. 37			12, 372. 35		
		5, 510. 12 (3)			7, 920. 71 (8)	7, 994. 73 (20)	8, 640. 06 (15)	
3	18, 143. 36 [1]	18, 143. 40			12, 621. 68	12, 504. 80	11, 570. 82	
		5, 438. 74 (5)	6, 238. 58 (4)	7, 237. 10 (40)		7, 845. 35 (20)		
4	18, 381. 48 [3]	18, 381. 52	16, 024. 86	13, 813. 89		12, 742. 90		
		5, 181. 86 (40 II)	5, 902. 94 (15 III)	6, 789. 27 (20)		7, 321. 76 (2)		
5	19, 292. 68 [3]	19, 292. 73	16, 936. 03	14, 725. 07		13, 654. 17		
		5, 051. 32 (3)				7, 063. 83 (20)	7, 562. 93 (8)	9, 250. 27 (3)
6	19, 791. 27 [1]	19, 791. 30				14, 152. 73	13, 218. 76	10, 807. 54
			5, 373. 86 (20 III)	6, 098. 67 (3 V)				
7	20, 960. 07 [4]		18, 603. 44	16, 392. 49				
		4, 598. 80 (25 III)	5, 157. 96 (6)			6, 209. 42 (2)		
8	21, 738. 71 [2]	21, 738. 73	19, 382. 13			16, 100. 12		
		4, 452. 97 (4)	4, 975. 25 (25 III)					7, 423. 69 (3)
9	22, 450. 51 [2]	22, 450. 64	20, 093. 90					13, 466. 70
		4, 263. 41 (10 III)	4, 739. 82 (3)	5, 294. 87 (12 III)		5, 613. 27 (10 III)		
10	23, 448. 60 [3]	23, 448. 83	21, 091. 97	18, 880. 97		17, 810. 00		
		4, 228. 08 (6 III)		5, 240. 40 (1)		5, 552. 12 (40 III)		6, 818. 94 (40)
11	23, 644. 74 [3]	23, 644. 76		19, 077. 22		18, 006. 15		14, 661. 00
			4, 417. 90 (10 III)	4, 896. 32 (3)		5, 167. 42 (3)		
12	24, 985. 35 [3]		22, 628. 86 b	20, 417. 82 c		19, 346. 64		
		3, 968. 01 (3 V)				5, 112. 13 (6)	5, 368. 50 (1)	
13	25, 194. 46 [1]	25, 194. 45 a				19, 555. 88	18, 622. 01	
		3, 899. 93 (20 II)	4, 294. 77 (30 II)			4, 999. 68 (5)	5, 244. 68 (2)	
14	25, 634. 22 [2]	25, 634. 25	23, 277. 61			19, 995. 72	19, 061. 65	
		3, 829. 67 (3)	4, 209. 71 (8 III)				5, 118. 46 (2)	
15	26, 104. 50 [2]	26, 104. 53	23, 747. 94				19, 531. 70?	
		3, 800. 39 (10 IV?)	4, 174. 33 (50 II)	4, 598. 92 (20 V)		4, 837. 24 (20)		
16	26, 305. 74 [3]	26, 305. 65	23, 949. 21	21, 738. 16		20, 667. 19		
		3, 777. 64 (50 II)			4, 773. 72 (10)	4, 800. 50 (25 II)	5, 025. 91 (2)	5, 719. 18 (40 III)
17	26, 463. 92 [1]	26, 464. 06			20, 942. 49	20, 825. 36	19, 891. 36	17, 480. 19
		3, 682. 25 (200 II)	4, 032. 27 (6 III)			4, 647. 45 (1)	4, 858. 41 (8)	5, 503. 28 (1)
18	27, 149. 63 [2]	27, 149. 61	24, 792. 95			21, 511. 17	20, 577. 13	18, 165. 95
		3, 630. 86 (8 II)			4, 541. 70 (4)	4, 565. 94 (20 III)	4, 769. 36 (2)	5, 389. 33 (6)
19	27, 533. 80 [1]	27, 533. 86			22, 012. 04	21, 895. 18	20, 961. 33	18, 550. 04
			3, 968. 01 (3 V)	4, 349. 73 (4)				
20	27, 551. 06 [4]		25, 194. 45 a	22, 983. 49				
		3, 615. 05 (3)	3, 951. 81 (12 III)	4, 330. 27 (8 V)		4, 540. 92 (20 III)		
21	27, 654. 34 [3]	27, 654. 28	25, 297. 73	23, 086. 78		22, 015. 82		

TABLE 1.—*Classified lines in the Hf_1 spectrum*—Continued

		A 0.00 [2]	B 2,356.60 [3]	C 4,567.58 [4]	D 5,521.64 [0]	E 5,638.55 [2]	F 6,572.50 [1]	G 8,983.70 [2]
22	28, 047. 81 [1]	3, 564. 31 (3) 28, 047. 94			4, 438. 02 (20 III) 22, 526. 27	4, 461. 17 (15 III) 22, 409. 38	4, 655. 19 (30 III) 21, 475. 41	5, 243. 99 (15 III) 19, 064. 16
23	28, 267. 43 [2]	3, 536. 62 (30 II) 28, 267. 54	3, 858. 30 (20 V) 25, 910. 83			4, 417. 90 (10 III) 22, 628. 86 b	4, 608. 10 (10) 21, 694. 86	5, 184. 29 (2) 19, 283. 69
24	28, 583. 75 [3]	3, 497. 49 (150 II) 28, 583. 78	3, 811. 76 (8 III) 26, 227. 18	4, 162. 68 (4 V) 24, 016. 24		4, 356. 98 (3) 22, 945. 25		
25	28, 790. 28 [1]	3, 472. 38 (100 II) 28, 790. 48			4, 296. 41 (4) 23, 268. 72	4, 318. 13 (6 III) 23, 151. 68	4, 499. 65 (4) 22, 217. 74	5, 047. 45 (15 III) 19, 806. 48
26	29, 246. 62 [4]		3, 717. 80 (40 II) 26, 890. 01	4, 050. 88 (2) 24, 679. 05				
27	29, 401. 54 [2]	3, 400. 21 (8 II) 29, 401. 54	3, 696. 52 (5 III) 27, 044. 80				4, 379. 13 (3d) 22, 829. 19	4, 896. 32 (3) 20, 417. 82 c
28	29, 752. 86 [2]	3, 360. 06 (6 II) 29, 752. 86	3, 649. 09 (10 III) 27, 396. 32			4, 145. 76 (6 V) 24, 114. 25		
29	29, 996. 83 [3]	3, 332. 73 (200 II) 29, 996. 83	3, 616. 89 (30 II) 27, 640. 21	3, 931. 36 (10 V) 25, 429. 32		4, 104. 23 (3) 24, 358. 26		4, 757. 61 (6) 21, 013. 10
30	30, 733. 18 [4]		3, 523. 02 (60 II) 28, 376. 65	3, 820. 74 (50 III) 26, 165. 54				
31	31, 342. 58 [3]	3, 189. 63 (8 II) 31, 342. 57		3, 733. 78 (15 III) 26, 774. 93		3, 889. 33 (4 V) 25, 704. 11		
32	31, 610. 72 [2]	3, 162. 57 (80 II) 31, 610. 73	3, 417. 35 (6 II) 29, 254. 08			3, 849. 17 (25 V) 25, 972. 29		4, 418. 25 (4) 22, 627. 06
33	31, 943. 24 [4]		3, 378. 93 (5d II) 29, 586. 70	3, 651. 85 (5) 27, 375. 61				
34	32, 533. 33 [2]	3, 072. 88 (300 II) 32, 533. 34	3, 312. 87 (100 II) 30, 176. 65					4, 245. 15 (5) 23, 549. 69
35	33, 121. 43 [2]	3, 018. 32 (80 II) 33, 121. 39	3, 249. 53 (12 II) 30, 764. 84			3, 637. 59 (2) 27, 482. 92		
36	33, 139. 11 [3]	3, 016. 71 (30 III) 33, 139. 07	3, 247. 66 (20 II) 30, 782. 55	3, 498. 99 (2) 28, 571. 53				
37	33, 538. 10 [2]	2, 980. 82 (100 II) 33, 538. 06	3, 206. 11 (25 II) 31, 181. 47			3, 583. 27 (2) 27, 899. 53	3, 707. 36 (2) 26, 965. 73	
38	33, 909. 34 [4]		3, 168. 39 (20 IV) 31, 552. 67	3, 407. 13 (2 V) 29, 341. 83				
39	33, 949. 23 [3]	2, 944. 71 (15 III) 33, 949. 30	3, 164. 39 (12 III) 31, 592. 55	3, 402. 51 (6 III) 29, 381. 67 d		3, 531. 23 (2) 28, 310. 68		
40	33, 994. 75 [3]	2, 940. 77 (200 II) 33, 994. 79	3, 159. 83 (30 II) 31, 638. 14	3, 397. 26 (8 II) 29, 427. 07		3, 525. 55 (2) 28, 356. 29		
41	34, 277. 79 [2]	2, 916. 49 (300 II) 34, 277. 78	3, 131. 81 (150 III) 31, 921. 20					

		2, 889. 62 (80 II)			3, 438. 43 (5 IV)	3, 452. 31 (4 V)	3, 567. 36 (6 V)	
42	34, 596. 46 [1]	34, 596. 51			29, 074. 74	28, 957. 85	28, 023. 96	
			3, 080. 84 (80 II)	3, 306. 12 (10 II)				
43	34, 805. 86 [4]		32, 449. 29	30, 238. 26				
		2, 866. 38 (150 II)	3, 074. 09 (10 IV)			3, 419. 18 (12 II)		3, 860. 91 (3)
44	34, 877. 03 [2]	34, 877. 00	32, 520. 53			29, 238. 42		25, 893. 31
		2, 860. 56 (10 V)	3, 067. 41 (80 II)					3, 850. 34 (1)
45	34, 947. 95 [2]	34, 947. 95	32, 591. 35					25, 964. 40
		2, 819. 75 (8 V)	3, 020. 54 (100 II)	3, 236. 77 (8 V)		3, 353. 03 (1)		
46	35, 453. 71 [3]	35, 453. 72	33, 097. 05	30, 886. 12		29, 815. 23		
			2, 964. 88 (150 II)	3, 172. 94 (100 II)				
47	36, 074. 98 [4]		33, 718. 36	31, 507. 43				
		2, 758. 76 (6 V)	2, 950. 68 (125 II)	3, 156. 68 (50 II)		3, 267. 17 (5 V)		3, 668. 20 (2)
48	36, 237. 32 [3]	36, 237. 48	33, 880. 62	31, 669. 72		30, 598. 74		27, 253. 59
		2, 730. 71 (2 V)	2, 918. 58 (80 III)	3, 119. 97 (10 IV)		3, 227. 87 (2 V)		
49	36, 609. 82 [3]	36, 609. 69	34, 253. 24	32, 042. 33		30, 971. 27		
		2, 718. 57 (8 V)	2, 904. 76 (80 II)			3, 210. 97 (8 III)	3, 310. 27 (25 II)	3, 597. 50 (3)
50	36, 772. 90 [2]	36, 773. 17	34, 416. 20			31, 134. 27	30, 200. 36	27, 789. 18
			2, 898. 26 (125 II)	3, 096. 76 (15 II)				
51	36, 850. 02 [4]		34, 493. 38	32, 282. 47				
		2, 697. 07 (2)				3, 181. 02 (15 II)		
52	37, 066. 1 [2]	37, 066. 29 ?				31, 427. 40		
			2, 867. 69 (2)			3, 165. 73 (3 V)		
53	37, 217. 70 [3]		34, 861. 06			31, 579. 18		
		2, 608. 47 (5)	2, 779. 36 (20 IV)				3, 148. 41 (15 IV)	3, 407. 13 (2)
54	38, 325. 41 [2]	38, 325. 21	35, 968. 91				31, 752. 90	29, 341. 83 d
		2, 602. 86 (2)	2, 773. 01 (8 V)	2, 954. 21 (100 II)		3, 050. 76 (60 II)		3, 397. 60 (6 V)
55	38, 407. 80 [3]	38, 407. 81	36, 051. 27	33, 840. 14		32, 769. 22		29, 424. 13
			2, 729. 10 (2)	2, 904. 42 (80 III)				
56	38, 987. 84 [4]		36, 631. 29	34, 420. 22				
			2, 713. 84 (6 V)	2, 887. 13 (15 V)		2, 979. 28 (8 V)		3, 309. 20 (3 V)
57	39, 193. 88 [3]		36, 837. 26	34, 626. 34		33, 555. 39		30, 210. 12
			2, 696. 18 (4 V)			2, 958. 02 (40 III)	3, 042. 09 (1)	
58	39, 435. 11 [2]		37, 078. 53			33, 796. 55	32, 862. 60	
		2, 487. 16 (3)	2, 642. 07 (3 V)				2, 973. 38 (6 V)	
59	40, 194. 43 [2]	40, 194. 37	37, 837. 85				33, 621. 97	
		2, 482. 67 (2)	2, 637. 00 (3)				2, 966. 95 (40 III)	
60	40, 267. 20 [2]	40, 267. 06	37, 910. 60				33, 694. 83	
					2, 841. 49 (2 V)	2, 850. 96 (25 V)	2, 928. 98 (2 V)	3, 151. 63 (6 V)
61	40, 704. 14 [1]				35, 182. 48	35, 065. 62	34, 131. 62	31, 720. 46
			2, 602. 68 (3)	2, 761. 62 (30 V)		2, 845. 83 (20 V)		
62	40, 767. 3 [3]		38, 410. 47	36, 199. 96		35, 128. 83		
			2, 502. 66 (3)			2, 726. 69 (2 V)		
63	42, 302. 14 [3]		39, 945. 45			36, 663. 67		

a, b, c, d=lines used twice.

The Hf atom has 72 electrons ($Z=72$), but only 4 are concerned with the production of the first optical spectrum. The 4 valence electrons are normally in $5d$ and $6s$ orbits, either d^2s^2 or d^3s. According to Hund's theory,[4] these configurations of valence electrons can produce the following low-energy spectral terms:

Electron configuration	Spectral terms		
d^2s^2		$^3F_{2,\ 3,\ 4}$	$^3P_{0,\ 1,\ 2}$
	$^1G_4$	$^1D_2$	$^1S_0$
d^3s		$^5F_{1,\ 2,\ 3,\ 4,\ 5}$	$^5P_{1,\ 2,\ 3}$
		$^3F_{2,\ 3,\ 4}$	$^5P_{1,\ 2,\ 3}$
		$^3F_{2,\ 3,\ 4}$	$^3P_{0,\ 1,\ 2}$
	$^3H_{4,\ 5,\ 6}$	$^3G_{3,\ 4,\ 5}$	$^3F_{2,\ 3,\ 4}$
	$^3D_{1,\ 2,\ 3}$	$^3D_{1,\ 2,\ 3}$	$^3P_{0,\ 1,\ 2}$
	$^1H_5$	$^1G_4$	$^1F_3$
	$^1D_2$	$^1D_2$	$^1P_1$

The total number of levels thus predicted is 47, nearly seven times as many as we have found. Comparison with the analogous Ti_I and Zr_I spectra which have been very completely analyzed by Russell [5] and by Kiess,[6] respectively, shows, however, that only a small part of these theoretical levels are important in the production of the strongest lines. For purposes of comparison and discussion the low terms of the three spectra are collected in Table 2.

TABLE 2.—*Low levels in Ti_I, Zr_I, and Hf_I spectra*

	Ti_I	Zr_I	Hf_I
$^3F_2$	0. 00	0. 00	0. 00
$^3F_3$	170. 14	570. 41	2, 356. 60
$^3F_4$	386. 88	1, 240. 84	4, 567. 58
$^1D_2$	7, 255. 29	—54. 70	5, 638. 55
$^3P'_0$	8, 436. 69	4, 196. 85	5, 521. 64
$^3P'_1$	8, 492. 48	4, 376. 28	6, 572. 50
$^3P'_2$	8, 602. 42	4, 186. 11	8, 983. 70
$^5F'_1$	6, 556. 86	4, 870. 53	
$^5F'_2$	6, 598. 83	5, 023. 41	
$^5F'_3$	6, 661. 00	5, 249. 07	
$^5F'_4$	6, 742. 79	5, 540. 54	
$^5F'_5$	6, 843. 00	5, 888. 93	

The identification of the Hf_I levels is only tentative; it was suggested by comparison with the analogous Ti_I and Zr_I spectra. In each case a triplet F term is involved in the production of the strongest lines; in the Ti_I spectrum, $^3F_2$ represents the normal state (zero excitation energy) of the atom. In Zr_I a singlet-D term is (slightly) lower than $^3F_2$, and in Hf_I we may thus expect to find $^1D_2$ considerably

[4] Hund, Linienspektren und periodisches System der Elemente, p. 158, Julius Springer, Berlin; 1927.
[5] Russell, Astrophys. J., 66, p. 388; 1927.
[6] Kiess, unpublished.

lower than $^3F_2$. In our Hf_{II} paper, attention was called to a similar tendency of the doublet-D term in the analogous spark spectra, Ti_{III}, Zr_{III}, Hf_{III}. Although a lower singlet-D term in the Hf_I spectrum has been sought, it has thus far evaded us.

In Ti_I the intervals between the sublevels of ^3F are $^3F_3-{}^3F_2=170$, $^3F_4-{}^3F_3=217$, which are exactly in the ratio of 3 to 4, in agreement with Landé's interval rule.[7] This interval rule is not strictly fulfilled in Zr_I, where the intervals in question are 570 and 670, and the deviation becomes still greater in Hf_I, with intervals 2,356.6 and 2,211.0. If, however, the sums of the intervals or range of ^3F levels in the three spectra are compared, we find Zr/Ti = 3.2 and Hf/Zr = 3.6, which leads us to believe that our interpretation of the first three levels (A. B. C. . . .) in the Hf_I spectrum may be correct.

In general, low or metastable ^3P terms in complex spectra follow the interval rule fairly closely. Thus in Ti_I the ratio $^3P_1-{}^3P_0/{}^3P_2-{}^3P_1$ is almost exactly 1 : 2. Zr_I appears to offer an exception, but we are nevertheless inclined to interpret our levels D, F, G in the Hf_I spectrum as ^3P, since the inner quantum numbers appear to be 0, 1, 2, and the intervals are in the ratio 1 : 2.1.

The remaining level, E, may be interpreted as a singlet-D level, although probably not the lowest one of this type. A quintet-F term provides some important metastable levels in both the Ti_I and Zr_I spectra, but we have been unable thus far to find the homologous term in the Hf_I spectrum. In the absence of Zeeman effects, no attempt is made to name any of the higher terms of the Hf_I spectrum. The authors plan to investigate the magnetic resolution of the Hf lines, but on account of the abnormal magnetic splitting factors (g) which may be expected we are not optimistic about the value of such observations except for identifying the low-energy levels.

WASHINGTON, November 16, 1929.

[7] Landé, Zeitschr. f. Phys., **15**, p. 189; 1923.

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